

RAMAN SPECTRA AND CONFORMATIONS OF *n*-HEXADECYNOIC FATTY ACIDS AND THEIR POTASSIUM SALTS

M. VAN DE VEN, H. VAN LANGEN, W. VERWER and Y.K. LEVINE*

Biophysics Department, Physics Laboratory, University of Utrecht, Princetonplein 5, 3584 CC Utrecht (The Netherlands)

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Raman spectra of *n*-hexadecynoic fatty acids, $\text{CH}_3(\text{CH}_2)_{m-2}\text{C}\equiv\text{C}(\text{CH}_2)_{n-2}\text{COOH}$ (with $n = 4, 6, 7, 8$ and 12 , $m + n = 16$) and their potassium salts were recorded and assigned. The skeletal optical mode (SOM) regions were analysed on using the dispersion curve of the ν_4 (stretch) vibrations of saturated fatty acids. The localised vibrations of the carboxyl- and methyl-terminated sections of the hydrocarbon chains were assigned to the phase differences $\delta = k\pi/m$ and $k\pi/n$ ($k = 1, 2, \dots$), respectively. Evidence for a ν_4 vibration with $\delta = \pi/2m$ was found. The materials were found to be resistant to chemical decomposition under laser illumination.

Keywords: *n*-hexadecynoic acids; potassium *n*-hexadecynoates; vibrational spectroscopy; unsaturated lipids.

Introduction

In recent years there has been a growing interest in the application of Raman spectroscopy to structural studies of biological membranes and lipid bilayers. In particular, much attention has been paid to the analysis of the conformation of the hydrocarbon chains of the lipids and their interchain interactions. To this end both protonated and perdeuterated molecules have been used. Furthermore, specifically deuterated chains have been studied in order to obtain structural information at different locations along the lipid chains.

Spatial resolution along the length of a lipid chain may also be achieved by another stratagem, the introduction of rigid defect structures into polymethylene chains [1,2] which decouple the vibrational modes of adjacent chain sections. Unsaturated olefinic double bonds are one such possibility [2]. However, olefinic linkages are susceptible to oxidation and cannot easily be introduced at arbitrary positions along fatty acid chains. In contrast, the chemical synthesis of fatty acid chains containing acetylenic linkages, triple

*To whom all correspondence should be addressed.

bonds, is fairly straightforward. These compounds also appear to be chemically stable, presumably because no hydrogen atoms are directly bonded to an 'unsaturated' carbon atom.

We have investigated the feasibility of such an approach by studying the Raman spectra of *n*-hexadecynoic acids and their respective potassium salts as a function of the position of the acetylenic linkage along the length of the chains. Here we present the assignment of the more important Raman lines together with a detailed analysis of the SOM region. The results show that the stiff acetylenic bonds indeed effectively decouple the vibrations of the carboxyl- and methyl-terminated chain sections. It may thus prove useful to synthesize Raman probes, in which perdeuterated alkyl segments are joined to protonated ones by a triple acetylenic bond, thereby enhancing further the spatial resolution along the chain.

Materials

ω -Bromoacids and 1-alkynes were obtained from Sigma. Potassium hydroxide (KOH), petroleum ether and methanol were purchased from Baker (AR). Doubly distilled water was used throughout.

The *n*-hexadecynoic acids were prepared by alkylation of the bromoacids with the appropriate 1-alkynes [1–3]. The reaction product was distilled and recrystallized several times from petroleum ether.

Potassium *n*-hexadecynoates were prepared from the corresponding *n*-hexadecynoic acid and potassium hydroxide. The KOH solution was slowly added stoichiometrically to 20 mg acid in methanol under a nitrogen gas atmosphere at room temperature and stirred continuously. Both acids and soaps were dried and stored under N₂ at 4°C. An analysis for purity was carried out by thin-layer chromatography. Raman spectra were recorded after pre-illuminating all samples, sealed in melting point capillaries, for at least 3 h with the laser power at the sample position, gradually increasing to 500 mW in order to reduce the fluorescence background.

Raman set-up

The Raman set-up is shown in Fig. 1. Spectra were obtained using an Ar ion-laser (Coherent model CR 18-UV) at 528 nm. An Anaspec-300S pre-monochromator filtered the plasma lines. The laser beam was focussed on the sample, with a 101-mm focal length lens. The laser power at the sample position was 500 mW, measured with a Coherent model 210 power meter. A 90° detection geometry was used and the scattered radiation was passed through a Jobin-Yvon Ramanor HG-2S double monochromator, equipped with a polarization scrambler and concave holographic gratings (110 ×

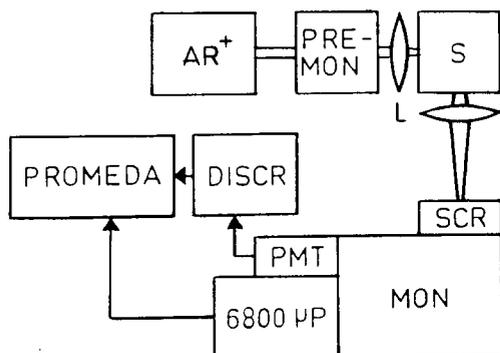


Fig. 1. Raman set-up. Ar⁺-Argon ion laser; PREMON, premonochromator; L, lenses; S, sample; SCR, polarization scrambler; MON, double monochromator; PMT, photomultiplier tube; 6800 μ P, microprocessor; DISCR, discriminator; PROMEDA, microcomputer; for details see text.

110 mm, 2000 grooves/mm), to a Peltier-cooled, red-sensitive RCA 31034 A-02 PM tube operating at -25°C and a cathode voltage of -1800 V .

The PM tube signal was first processed by an STD-N-2 snap-off timing discriminator (Elsint) and then stored in a Promeda microcomputer (Elsint). Net count rates were monitored with an HP 5383A 520 MHz frequency counter. The double monochromator was driven by a home-made microcomputer based on a 6800 microprocessor.

All spectra were the average of four scans (scan speed 200 cm^{-1} per min) at a slit width of $200\text{ }\mu\text{m}$ (1.5 cm^{-1} at 18914 cm^{-1}) and were recorded at a temperature of 20°C . The absolute accuracy of all line positions is 2 cm^{-1} . The spectral sensitivity of the Raman set-up was wavelength independent to within 5% over the spectral range of $0\text{--}3100\text{ cm}^{-1}$ as measured relative to the laser line. The relative line intensities in the spectra are thus comparable.

Results

Assignment of the Raman bands

Figures 2–6 show the Raman spectra of 4-, 6-, 7-, 8- and 12-*n*-hexadecynoic acids and potassium hexadecynoates. A tentative assignment of the more important Raman bands of the acids and salts is given in Tables I and II. The bands can be attributed to four different groups present in the compounds: the carboxylic head group, the polymethylene chains, the central acetylene segment and the methyl end group. For the assignment of the Raman lines the spectral data of polyethylene [6], *n*-hexadecanoic acid [1,7], *cis*- and *trans*-9-hexadecanoic acid [2], adipic acid [8], 2-butyne,

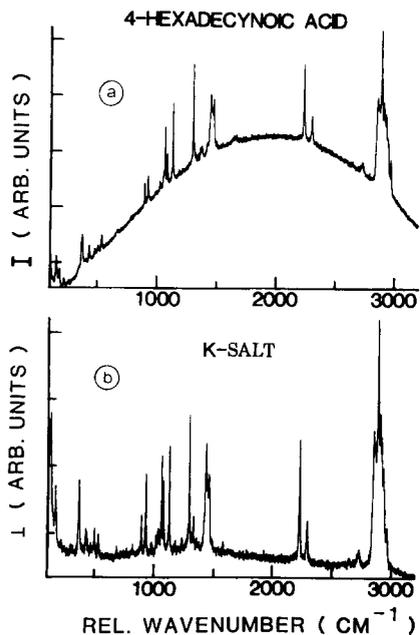


Fig.2. Raman spectrum of (a) 4-*n*-hexadecynoic acid and (b) potassium-4-*n*-hexadecynoate recorded at a temperature of 20°C.

2-pentyne and 3-hexyne [9], and several other alkyl-acetylenes [10,11] together with those for anionic soaps [12,13] were used. The assignments were also checked using normal coordinate calculations of polymethylene chains [14–16] and adipic acid crystals [8].

(i) *Disubstituted-acetylene group*

The alkyl-acetylene group exhibits two (very) strong, well-separated lines in the Raman spectra of all the acids and salts. The lines around 2220–2230 cm^{-1} and 2287–2295 cm^{-1} (acids) or 2286–2290 cm^{-1} (salts) were both assigned to the $\nu(\text{C}\equiv\text{C})$ stretch mode, which is in Fermi resonance with the anti-symmetric stretch vibration $\nu_a(\text{C}-\text{C}\equiv\text{C}-\text{C})$ [9,21]. Here $2\nu_a(\text{C}-\text{C}\equiv\text{C}-\text{C}) \approx \nu(\text{C}\equiv\text{C})$. A strong band near 370 cm^{-1} can be assigned to the deformation vibration $\delta(\text{C}-\text{C}\equiv\text{C}-\text{C})$ [10,22].

(ii) *Carboxyl group*

Weak and broad Raman bands arising from the carboxylic head groups were found between 1640 and 1650 cm^{-1} for all the acids and for the potassium-4,7-*n*-hexadecynoates. For the other hexadecynoates the signal-to-noise ratio was too low to observe the lines. These bands could be

TABLE I

 ASSIGNMENTS OF THE RAMAN BANDS OF THE HEXADECYNOIC ACIDS:
 $\text{CH}_3(\text{CH}_2)_{m-2}\text{C}\equiv\text{C}(\text{CH}_2)_{n-2}\text{COOH}$ ($m + n = 16$)

Raman bands (cm^{-1})					Assignments
$n = 4$	$n = 6$	$n = 7$	$n = 8$	$n = 12$	
		101, <i>s</i>	105, <i>vw</i>		
		118, <i>w</i>		121, <i>m</i>	
			129, <i>vs</i>		
	136, <i>s</i>				
		144, <i>w</i>		149, <i>w</i>	
158, <i>m</i>	160, <i>m,b</i>	165, <i>w</i>		165, <i>w</i>	
182, <i>m</i>		182, <i>w</i>	175, <i>vw</i>	185, <i>vw</i>	
		206, <i>vw</i>	205, <i>w</i>		
220, <i>w</i>				219, <i>vw</i>	
	230, <i>s</i>	235, <i>vw,b</i>			
260, <i>vw</i>		269, <i>m</i>	268, <i>w,sh</i>		
			285, <i>s</i>		
		301, <i>w</i>	305, <i>w,sh</i>		
330, <i>vw,sh</i>					
	335, <i>m</i>	340, <i>m</i>			
350, <i>vw,sh</i>				359, <i>m,sh</i>	
371, <i>s</i>	374, <i>vs</i>	375, <i>vs</i>	373, <i>vs</i>	378, <i>s</i>	$\delta(\text{C}-\text{C}\equiv\text{C})$ deformation
	387, <i>m,sh</i>				
395, <i>vw</i>				393, <i>m</i>	
407, <i>vw</i>			406, <i>w</i>		
431, <i>m</i>	430, <i>m</i>	444, <i>s</i>	422, <i>m</i>	459, <i>m</i>	
			466, <i>m</i>	465, <i>w,sh</i>	
476, <i>w</i>				480, <i>vw?</i>	
	485, <i>w</i>	489, <i>m</i>	490, <i>w</i>	496, <i>w</i>	
503, <i>w</i>					$\delta(\text{C}-\text{C}-\text{O})$ deformation
	521, <i>s</i>		524, <i>s</i>		
533, <i>m</i>		530, <i>s</i>		532, <i>vw</i>	
			542, <i>vw</i>	569, <i>m</i>	
	630, <i>w</i>				
660, <i>vw</i>	663, <i>w</i>	665, <i>vw</i>	665, <i>vw</i>		$\delta(\text{O}=\text{C}-\text{O})$ in-plane-deformation
	720, <i>vw</i>	730, <i>w</i>		738, <i>vw</i>	
770, <i>vw</i>	783, <i>vw</i>	760, <i>vw</i>			
	800, <i>vw</i>	800, <i>vw</i>		806, <i>vw</i>	} $r(\text{CH}_2) + t(\text{CH}_2), \nu_8$
	815, <i>vw</i>	825, <i>vw</i>		835, <i>vw</i>	
		850, <i>vw</i>		859, <i>w</i>	
891, <i>m</i>	889, <i>s</i>	891, <i>s</i>	890, <i>s</i>	894, <i>s</i>	
		895, <i>w,sh</i>			
	904, <i>m</i>		907, <i>m</i>		$\nu(\text{C}-\text{COOH})$
918, <i>m</i>	915, <i>w,sh</i>	910, <i>m</i>		910, <i>m</i>	
		933, <i>w</i>			$r(\text{CH}_2) + t(\text{CH}_2), \nu_8$
983, <i>vw</i>		980, <i>w</i>	980, <i>w</i>	988, <i>w</i>	
993, <i>vw</i>	992, <i>vw</i>	993, <i>m</i>	992, <i>w</i>		
		1002, <i>w,sh</i>			
1018, <i>w</i>	1022, <i>m</i>		1020, <i>w,sh</i>	1015, <i>vw</i>	
1036, <i>vw,sh</i>		1036, <i>m</i>	1031, <i>s</i>	1036, <i>w</i>	
1046, <i>m,sh</i>	1047, <i>s,sh</i>	1046, <i>s</i>	1047, <i>s,sh</i>		

TABLE I (continued)

Raman bands (cm ⁻¹)					Assignments
<i>n</i> = 4	<i>n</i> = 6	<i>n</i> = 7	<i>n</i> = 8	<i>n</i> = 12	
1055, <i>m, sh</i>	1055, <i>vs</i>	1059, <i>s</i>	1060, <i>vs</i>	1058, <i>m, sh</i>	$\nu(\text{C-C}) + \delta(\text{C-C-C}), \nu_4(\delta \sim \pi)$
1062, <i>vs</i>	1060, <i>vs</i>	1064, <i>m, sh</i>	1070, <i>m</i>	1067, <i>vs</i>	
1079, <i>s</i>	1076, <i>s</i>	1080, <i>vs</i>	1080, <i>vs</i>	1089, <i>vs</i>	
		1110, <i>w, sh</i>		1101, <i>s, sh</i>	
				1110, <i>vs</i>	
1127, <i>vs</i>	1124, <i>vs</i>	1121, <i>vs</i>	1118, <i>vs</i>		$\nu(\text{C-C}) + \delta(\text{C-C-C}), \nu_4(\delta \sim 0)$
1185, <i>vw</i>	1183, <i>vw</i>	1180, <i>vw</i>			$t(\text{CH}_2) + r(\text{CH}_2), \nu_7(\delta \sim 0)$
1215, <i>vw</i>	1215, <i>vw</i>		1218, <i>vw</i>	1205, <i>vw, b</i>	
	1249, <i>vw</i>	1240, <i>vw</i>		1230, <i>vw</i>	
				1262, <i>w</i>	
		1271, <i>m, b</i>		1285, <i>m, sh</i>	
1295, <i>vs</i>	1296, <i>vs</i>	1296, <i>vs</i>	1296, <i>vs</i>	1300, <i>vs</i>	$t(\text{CH}_2) + r(\text{CH}_2), \nu_7(\delta \sim \pi)$
		1307, <i>s</i>			
1318, <i>w</i>	1315, <i>w, sh</i>	1334, <i>m</i>		1332, <i>vs</i>	
1340, <i>w</i>	1340, <i>w</i>	1342, <i>w</i>	1348, <i>m</i>		
1356, <i>w</i>	1356, <i>w</i>	1351, <i>vw</i>		1354, <i>w</i>	
1369, <i>w</i>		1363, <i>vw</i>	1363, <i>m</i>		$\text{CH}_3, \delta_s(\text{C-H})$
				1372, <i>w</i>	
1403, <i>vw, sh</i>	1408, <i>w</i>		1405, <i>w</i>		$w(\text{CH}_2)$
1412, <i>w, sh</i>		1410, <i>w</i>	1415, <i>s, sh</i>	1414, <i>m</i>	$w(\text{CH}_2), \nu_3(\delta \sim \pi)$
		1427, <i>s</i>	1422, <i>vs</i>		
1432, <i>s</i>	1431, <i>vs</i>			1430, <i>s, sh</i>	
1445, <i>vs</i>	1441, <i>vs</i>	1440, <i>vs, sh</i>	1439, <i>vs</i>		$s(\text{CH}_2), \nu_2(\delta \sim 0)$
		1448, <i>vs</i>		1441, <i>vs</i>	
1460, <i>s</i>		1450, <i>vs, sh</i>	1458, <i>vs, sh</i>	1455, <i>vs, sh</i>	
1467, <i>s</i>	1462, <i>vs</i>	1466, <i>vs</i>		1465, <i>s, sh</i>	
	1480, <i>s</i>		1470, <i>vs, sh</i>	1475, <i>s, sh</i>	
		1489, <i>w</i>	1485, <i>w, sh</i>		$\delta(\text{CH}_3)$
1490, <i>w</i>				1508, <i>vw</i>	
	1532, <i>vw</i>				
		1550, <i>vw</i>			
			1570, <i>vw</i>	1575, <i>vw</i>	
1643, <i>vw, b</i>	1648, <i>w, b</i>	1640, <i>w, b</i>	1645, <i>w, b</i>	1654, <i>w, b</i>	$\nu(\text{C=O})$ stretch
2228, <i>vs</i>	2226, <i>vs</i>	2222, <i>vs</i>	2225, <i>vs</i>	2231, <i>vs</i>	$\nu(\text{C}\equiv\text{C})$ stretch + $2\nu_a(\text{C-C}\equiv\text{C-C})$
2294, <i>m</i>	2292, <i>s</i>	2287, <i>s</i>	2292, <i>s</i>	2295, <i>s</i>	
2575, <i>vw</i>					
2600, <i>vw</i>	2615, <i>vw</i>				
2635, <i>vw, sh</i>				2650, <i>vw</i>	
2700, <i>vw</i>	2680, <i>vw</i>	2700, <i>vw</i>	2675, <i>vw</i>	2688, <i>vw</i>	Combination band $s(\text{CH}_2) + t(\text{CH}_2)$
2721, <i>w, b</i>	2718, <i>w, b</i>	2727, <i>w, b</i>	2720, <i>w, b</i>	2727, <i>w, b</i>	
2828, <i>s</i>					
	2830, <i>vs, sh</i>		2827, <i>s, sh</i>		
2845, <i>vs</i>	2845, <i>vs</i>	2840, <i>s, sh</i>	2842, <i>vs</i>		$\text{CH}_2, \nu_3(\text{C-H})$
2857, <i>vs</i>			2855, <i>vs</i>	2850, <i>vs</i>	
	2860, <i>vs</i>	2860, <i>vs, sh</i>	2865, <i>vs</i>	2865, <i>vs, sh</i>	
2870, <i>vs, sh</i>	2870, <i>vs</i>	2870, <i>vs</i>		2875, <i>vs, sh</i>	$\text{CH}_3, \nu_1(\text{C-H})$
2880, <i>vs</i>	2880, <i>vs</i>	2875, <i>vs</i>	2882, <i>vs</i>	2880, <i>vs</i>	$\text{CH}_2, \nu_a(\text{C-H})$
2887, <i>vs, sh</i>					
2895, <i>vs</i>	2893, <i>vs</i>		2895, <i>vs</i>	2895, <i>vs, sh</i>	$\omega(\text{CH}_2), \nu_a(\text{C-H})$

TABLE I (continued)

Raman bands (cm^{-1})					Assignments
$n = 4$	$n = 6$	$n = 7$	$n = 8$	$n = 12$	
2905, <i>vs, sh</i>	2903, <i>vs</i>	2900, <i>vs</i>	2905, <i>vs</i>	2905, <i>vs</i>	$\text{CH}_2, \nu_a(\text{C-H})$ $\alpha\text{-CH}_2, \nu_a(\text{C-H})$
2917, <i>vs</i>	2915, <i>vs, sh</i>	2915, <i>vs, sh</i>	2910, <i>vs, sh</i>	2920, <i>vs, sh</i>	
2933, <i>s, sh</i>	2933, <i>vs</i>	2933, <i>s, sh</i>		2935, <i>vs</i>	$\text{CH}_3, \nu_a(\text{C-H})$ o.p. $\text{CH}_3, \nu_a(\text{C-H})$ i.p.
2955, <i>m, sh</i>	2953, <i>s</i>	2950, <i>s</i>	2950, <i>s</i>		
2965, <i>s</i>	2963, <i>s</i>	2983, <i>m</i>	2960, <i>s</i>	2963, <i>vs</i> 3010, <i>w</i>	

assigned to the $\nu(\text{C}=\text{O})$ stretch vibration in analogy with the bands observed in the spectra of adipic acid and stearic acid [2,8]. The carboxyl stretch frequencies, $\nu(\text{C}-\text{COOH})$, were between 904 and 918 cm^{-1} and the $\delta(\text{O}=\text{C}-\text{O})$ in plane deformation was found to lie between 660 and 665 cm^{-1} . The $\delta(\text{C}-\text{C}-\text{O})$ deformation vibration was assigned to bands in the $520\text{--}530 \text{ cm}^{-1}$ region [2].

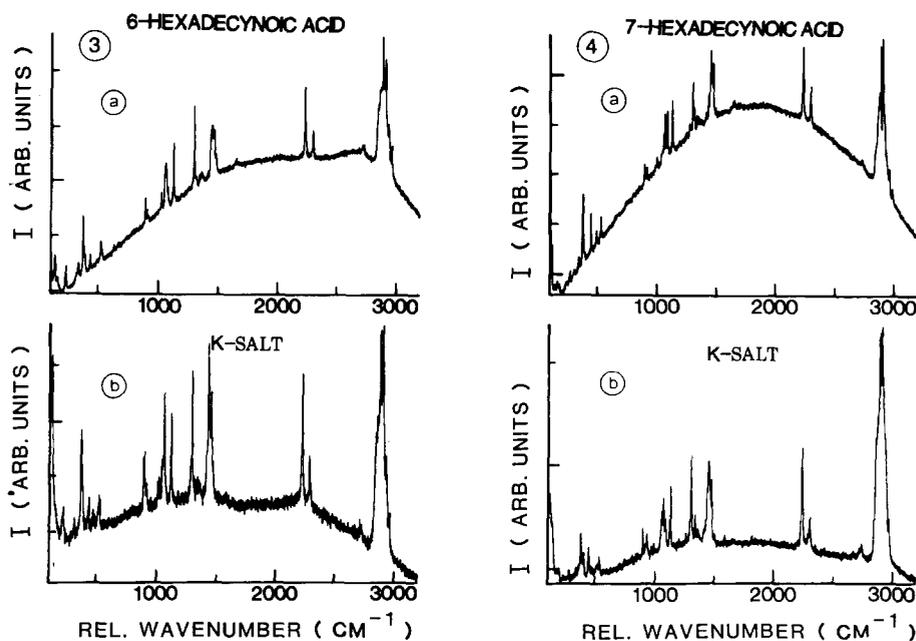


Fig. 3. Raman spectrum of (a) 6-*n*-hexadecynoic acid and (b) potassium-6-*n*-hexadecynoate taken at a temperature of 20°C .

Fig. 4. Raman spectrum of (a) 7-*n*-hexadecynoic acid and (b) potassium-7-*n*-hexadecynoate recorded at a temperature of 20°C .

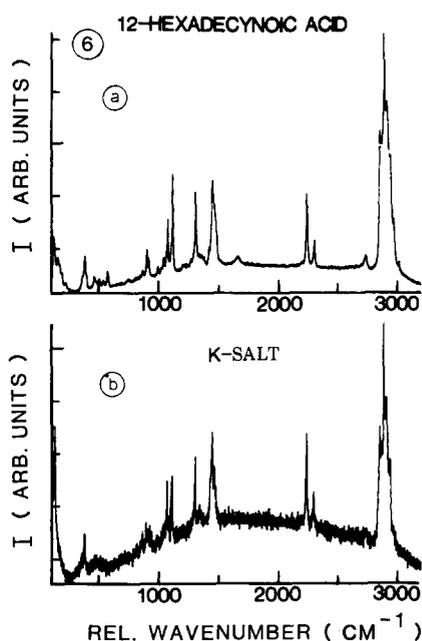
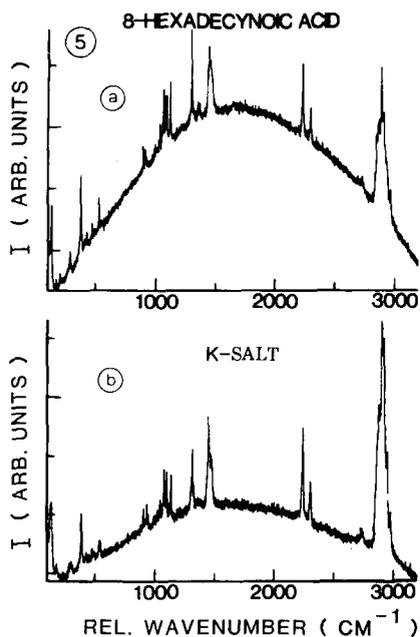


Fig. 5. Raman spectrum of (a) 8-*n*-hexadecyanoic acid and (b) potassium-8-*n*-hexadecyanoate recorded at a temperature of 20°C.

Fig. 6. Raman spectrum of (a) 12-*n*-hexadecyanoic acid and (b) potassium-12-*n*-hexadecyanoate taken at a temperature of 20°C.

(iii) Polymethylene chain and methyl end-group

Comparison of Figs. 2–6 with published Raman spectra of adipic acid [8] and stearic acid [2] shows that the CH, CH₂ and CH₃ vibrations can be easily correlated.

2700–3100 cm⁻¹. The assignment of bands in this spectral region is complicated due to the occurrence of Fermi resonances. Nevertheless assignments could be made for the hexadecyanoic acids and the potassium salts following published data on related compounds [7,23,24]. The frequency branches ν_6 and ν_1 are found in this spectral region [1]. ν_1 is the symmetric stretch mode and ν_6 the anti- or asymmetric vibration [23] of the CH₂ groups in a polymethylene chain. The asymmetric stretch of the terminal methyl groups $\nu_a(\text{C-H})$, the in-skeletal plane mode, was found between 2960–3010 cm⁻¹ [7,23–25] and the $\nu_a(\text{C-H})$, the out-of-skeletal plane mode, stretch vibration could be assigned to the lines near 2950 cm⁻¹. The antisymmetric stretch $\nu_a(\text{C-H})$ of the α -CH₂ group, located near the carboxylic head group, was not observed. The antisymmetric stretch, $\nu_a(\text{C-H})$ of the central CH₂ groups, was observed around 2915–2880 cm⁻¹. The $\nu_a(\text{C-H})$ vibration of the terminal CH₂ group might lie in the region 2900–2890 cm⁻¹, but the assignment is uncertain [7].

TABLE II

ASSIGNMENTS OF THE RAMAN BANDS OF THE HEXADECYNOATES:
 $\text{CH}_3(\text{CH}_2)_{m-2}\text{C}\equiv\text{C}(\text{CH}_2)_{n-2}\text{COOK}(m+n=16)$

Raman bands (cm^{-1})					Assignments
$n = 4$	$n = 6$	$n = 7$	$n = 8$	$n = 12$	
127, <i>s</i>	125, <i>s</i> 130, <i>vw</i>	107, <i>m</i> 132, <i>vw, sh</i>	124, <i>s</i>	122, <i>s</i> 148, <i>vw</i>	
172, <i>m</i> 180, <i>w, sh</i>		170, <i>vw</i>	171, <i>vw</i>		
218, <i>vw</i>	220, <i>w</i>	190, <i>vw</i> 222, <i>vw</i> 272, <i>vw</i>			
300, <i>vw</i> 316, <i>vw</i>	318, <i>vw</i>	312, <i>vw</i> 332, <i>vw</i> 352, <i>vw</i>	290, <i>w</i>	283, <i>vw</i>	
370, <i>s</i>	374, <i>s</i> 390, <i>m, sh</i> 408, <i>vw</i>	372, <i>m</i> 394, <i>w</i>	350, <i>vw, sh</i> 375, <i>s</i> 415, <i>vw</i>	353, <i>w, sh</i> 372, <i>m</i>	$\delta(\text{C}-\text{C}\equiv\text{C})$ deformation
426, <i>w</i> 435, <i>vw</i>	430, <i>w</i> 438, <i>w</i>	435, <i>w, sh</i> 440, <i>m</i>	439, <i>vw</i>	431, <i>vw</i>	
465, <i>vw?</i> 498, <i>w</i>	469, <i>vw</i> 487, <i>vw</i>	462, <i>vw</i>	465, <i>vw</i> 480, <i>vw</i>	451, <i>vw</i> 474, <i>vw</i>	
530, <i>w</i>	512, <i>w, sh</i> 525, <i>w</i>	505, <i>vw, b</i> 524, <i>w</i>	522, <i>w</i> 530, <i>w</i>	505, <i>vw</i>	$\delta(\text{C}-\text{C}-\text{O})$ deformation
605, <i>vw</i>	608, <i>vw</i>	562, <i>vw</i>		565, <i>s</i> 650, <i>m</i> 659, <i>w, sh</i>	
685, <i>vw</i>		730, <i>vw</i>			
768, <i>vw</i>	750, <i>vw</i>		760, <i>vw</i>		} $r(\text{CH}_2) + t(\text{CH}_2), \nu_8$
816, <i>vw, b</i>		802, <i>vw</i>		807, <i>vw</i> 823, <i>vw</i> 837, <i>vw</i> 855, <i>vw</i>	
		847, <i>vw</i>			
891, <i>m</i>	891, <i>m</i> 901, <i>m</i> 918, <i>w</i>	892, <i>m</i>	870, <i>vw</i> 892, <i>w</i>	888, <i>m</i>	$\nu(\text{C}-\text{COOK})$
927, <i>s</i>		916, <i>w, sh</i> 926, <i>w</i>	922, <i>w</i> 932, <i>vw</i>	918, <i>m</i> 930, <i>w</i>	} $r(\text{CH}_2) + t(\text{CH}_2), \nu_8$
975, <i>vw</i>	950, <i>vw</i> 980, <i>vw</i> 1008, <i>vw</i>	965, <i>vw</i> 984, <i>vw</i>	980, <i>vw</i> 990, <i>vw</i> 1007, <i>w</i>	984, <i>vw</i> 1005, <i>vw</i>	

TABLE II (continued)

Raman bands (cm ⁻¹)					Assignments
<i>n</i> = 4	<i>n</i> = 6	<i>n</i> = 7	<i>n</i> = 8	<i>n</i> = 12	
1015, <i>vw</i>	1021, <i>vw</i>				
1033, <i>w</i>		1035, <i>w, sh</i>	1032, <i>m</i>	1033, <i>vw</i>	
	1048, <i>m, sh</i>	1048, <i>m</i>	1053, <i>w, sh</i>		
1061, <i>vs</i>	1063, <i>s</i>	1063, <i>m</i>	1065, <i>s</i>	1063, <i>s</i>	$\nu(\text{C}-\text{C}) + \delta(\text{C}-\text{C}-\text{C}), \nu_4(\delta \sim \pi)$
1077, <i>s</i>	1075, <i>w, sh</i>			1073, <i>w, sh</i>	
		1081, <i>m</i>	1085, <i>s</i>		
			1098, <i>vw</i>	1102, <i>s</i>	
	1112, <i>vw, sh</i>	1115, <i>w, sh</i>		1114, <i>m, sh</i>	
1126, <i>vs</i>	1122, <i>s</i>	1123, <i>s</i>	1122, <i>m</i>	1121, <i>vw</i>	$\nu(\text{C}-\text{C}) + \delta(\text{C}-\text{C}-\text{C}), \nu_4(\delta \sim 0)$
1175, <i>vw</i>	1175, <i>vw</i>		1182, <i>vw</i>	1174, <i>vw</i>	$t(\text{CH}_2) + r(\text{CH}_2), \nu_7(\delta \sim 0)$
	1218, <i>vw</i>	1197, <i>vw</i>			
1230, <i>vw</i>					
	1268, <i>vw</i>	1250, <i>vw</i>			
1275, <i>vw, sh</i>	1270, <i>vw</i>				
	1280, <i>w, sh</i>		1285, <i>w, sh</i>	1287, <i>w, sh</i>	
1293, <i>vs</i>	1295, <i>vs</i>	1297, <i>vs</i>	1297, <i>s</i>	1295, <i>vs</i>	$t(\text{CH}_2) + r(\text{CH}_2), \nu_7(\delta \sim \pi)$
				1309, <i>w, sh</i>	
1315, <i>vw</i>	1315, <i>w, sh</i>		1312, <i>w</i>		
1330, <i>m</i>		1331, <i>m</i>		1333, <i>vw</i>	
	1340, <i>w</i>		1347, <i>vw, b</i>		
1355, <i>vw</i>	1360, <i>vw</i>	1355, <i>vw</i>		1367, <i>vw</i>	$\text{CH}_3, \delta_3(\text{C}-\text{H})$
		1405, <i>w, sh</i>			$w(\text{CH}_2), \nu_3(\delta \sim \pi)$
1418, <i>m, sh</i>	1422, <i>m, sh</i>		1420, <i>m, sh</i>	1419, <i>m, sh</i>	
1427, <i>s</i>		1429, <i>s</i>		1428, <i>s, sh</i>	
1436, <i>vs</i>	1435, <i>vs</i>		1434, <i>vs</i>	1435, <i>vs</i>	$s(\text{CH}_2), \nu_2(\delta \sim 0)$
1440, <i>s, sh</i>		1444, <i>vs</i>			
1453, <i>s, sh</i>	1456, <i>s</i>		1457, <i>s</i>	1453, <i>s, sh</i>	
1461, <i>s</i>		1468, <i>s</i>	1465, <i>m, sh</i>		
1477, <i>vw</i>	1475, <i>m</i>				$\delta(\text{CH}_3)$
		1495, <i>vw</i>			
1575, <i>vw</i>	1580, <i>vw</i>	1578, <i>vw</i>	1580, <i>vw</i>	1580, <i>vw</i>	
2224, <i>vs</i>	2223, <i>vs</i>	2226, <i>vs</i>	2225, <i>vs</i>	2225, <i>vs</i>	
2287, <i>m</i>	2286, <i>m</i>	2290, <i>m</i>	2289, <i>m</i>	2288, <i>m</i>	$\nu(\text{C} \equiv \text{C})$ stretch + $2\nu_4(\text{C}-\text{C} \equiv \text{C}-\text{C})$
2640, <i>vw</i>		2650, <i>vw</i>			
2720, <i>w, b</i>	2720, <i>vw, b</i>	2722, <i>w, b</i>	2720, <i>w, b</i>	2720, <i>w, b</i>	Combination band $s(\text{CH}_2) + t(\text{CH}_2)$
	2832, <i>s, sh</i>	2830, <i>s, sh</i>	2830, <i>s, sh</i>		
2848, <i>m, sh</i>	2843, <i>vs</i>	2848, <i>vs</i>	2845, <i>vs</i>	2843, <i>vs</i>	
2857, <i>vs</i>	2858, <i>vs</i>	2860, <i>vs</i>	2857, <i>vs</i>	2858, <i>s, sh</i>	
2875, <i>vs</i>	2870, <i>vs</i>	2880, <i>vs</i>	2870, <i>vs</i>	2877, <i>vs</i>	
2882, <i>vs</i>	2880, <i>vs</i>	2897, <i>vs</i>	2890, <i>vs</i>	2887, <i>vs</i>	
2900, <i>vs</i>	2900, <i>vs</i>		2903, <i>vs</i>	2899, <i>vs</i>	
2910, <i>vs</i>		2912, <i>vs, sh</i>	2918, <i>vs, sh</i>		
2926, <i>vs</i>		2930, <i>vs, sh</i>			
2935, <i>s, sh</i>	2938, <i>s, sh</i>		2932, <i>vs</i>	2932, <i>s</i>	
2956, <i>m</i>	2950, <i>s</i>	2956, <i>s</i>	2955, <i>m, sh</i>	2958, <i>m</i>	
			2963, <i>s</i>		

The symmetric stretch $\nu_s(\text{C-H})$ of the methyl end-group was observed near 2870 cm^{-1} , while a similar vibration around 2845 cm^{-1} could be assigned to the CH_2 groups. The bands between $2600\text{--}2727\text{ cm}^{-1}$ were attributed to a combination of the CH_2 scissoring mode at 1440 cm^{-1} and CH_2 twist modes near 1180 and 1295 cm^{-1} .

$500\text{--}1500\text{ cm}^{-1}$. The normal vibrations of the *trans*-chain consisting of n methylene units are usually characterised by the phase differences between the vibrations of adjacent units. This phase difference δ is defined as $\delta = k\pi/n$, $k = 0, 1, 2, \dots, n-1$. The symmetry of the vibrations determines which of the modes with δ approximately equal to 0 or π will give the highest intensity.

The frequency branches in this region are the bend (ν_2, δ), wag (ν_3, w), twist (ν_7, t) and rock (ν_8, r) modes of the *trans*-polymethylene chain [1]. However, according to Refs. 2, 7, 8 and 24, the CH_3 in-plane degenerate deformation, $\delta(\text{C-H})$, near 1480 cm^{-1} , and the CH_3 out-of-plane degenerate deformation around 1450 cm^{-1} [7] could also be present.

The bands between 1422 and 1470 cm^{-1} were assigned to the CH_2 scissoring, $s(\text{CH}_2)$, $\nu_2(\delta \sim 0)$ [2,7] and the $1403\text{--}1414\text{ cm}^{-1}$ region to the CH_2 wagging, $w(\text{CH}_2)$, with $\nu_3 \sim \pi$. Furthermore the $1360\text{--}1372\text{ cm}^{-1}$ region was attributed to the symmetric C-H bending $\delta_s(\text{C-H})$ of the terminal methyl group. The lines around 1295 cm^{-1} , $\nu_7(\delta \sim \pi)$, and the 1184 cm^{-1} region, $\nu_7(\delta \sim 0)$, arise from combination modes of CH_2 twist and rock: $t(\text{CH}_2) + r(\text{CH}_2)$.

The skeletal modes in the regions around 1126 cm^{-1} and 1064 cm^{-1} were respectively assigned to the $\nu_4(\delta \sim 0)$ branch and the $\nu_4(\delta \sim \pi)$ branch of the C-C stretch coupled to the C-C-C deformation [2] (see below). Many shoulders were observed near $1046, 1058$ and 1110 cm^{-1} in the acid spectra, and near 1050 and 1113 cm^{-1} for the salts. The frequencies of these shoulders were the same in all the compounds. These lines possibly reflect a different intra-chain environment for carbon atoms. The ν_8 branches of the CH_2 rock and CH_2 twist can possibly be related to the bands in the $926\text{--}993\text{ cm}^{-1}$ and the $720\text{--}859\text{ cm}^{-1}$ regions.

$0\text{--}500\text{ cm}^{-1}$. In this region many longitudinal acoustic (LA) modes are found (Figs. 2-6). Comparison of the spectral data of palmitic and palmitoleic acid [1] shows that owing to the presence of a double C=C bond in the C_{16} chain the analysis of this spectral region becomes much more complicated. A similar effect is observed for all the hexadecynoic acids and their potassium salts.

(iv) Skeletal vibrations

Since the SOM contain the most valuable information about the vibrations of the hydrocarbon chains, this spectral region will be discussed here in detail. The frequency-phase difference relation (dispersion curve) for the ν_4

branch of the SOM vibrations has been calculated and experimentally checked for a large number of *n*-paraffins [14–16]. Following Koyama et al. [2] we used the phase difference $\delta = k\pi/m$ ($k = 1, 2, \dots, n-1$) for the assignment of this branch for the saturated *n*-hexadecanoic acid.

For the unsaturated fatty acid $\text{CH}_3(\text{CH}_2)_{m-2}\text{C}\equiv\text{C}(\text{CH}_2)_{n-2}\text{COOH}$ (hereafter the *n/m* acid, with $m+n=16$) the phase differences $\delta = k\pi/m$ and $\delta = k\pi/n$ were used separately for each section of the chain. This is done because the central acetylene group may decouple the vibrations of the two sections. However, as the hydrocarbon chain can be regarded as having a free end (methyl group) and a semi-rigid end: the hydrogen-bonded carboxyl head group (acids) or the heavy COOK group (salts), a vibrational mode may exist with a node at the central acetylene group. We therefore also considered the phase difference $\delta = \pi/2m$, which would characterize this vibration of the methyl-terminated section.

The dispersion curve for hexadecanoic acid was used to assign the skeletal optical vibrations (ν_4) of the unsaturated hexadecynoic acids and their potassium salts. Since the $\text{C}\equiv\text{C}$ bond is much stiffer than the $\text{C}-\text{C}$ bond, it is assumed that the ν_4 vibrations are localized and that *no coupling* occurs between the methyl- and the carboxyl-terminated sections.

n-Hexadecynoic acids

The frequency-phase difference relation obtained for the carboxyl-terminated chain segments is shown in Fig. 7a (denoted by left-justified filled symbols) and listed in Table III. The very intense band observed near 1080 cm^{-1} in the spectrum of the 7/9 acid was assigned to $\delta/\pi = 1/7$. The weak band at 1002 cm^{-1} was assigned to $\delta/\pi = 2/7$. Similarly the strong band at 1076 cm^{-1} for the 6/10 acid was assigned to $\delta/\pi = 1/6$ and the very weak line at 992 cm^{-1} to $\delta/\pi = 2/6$.

Bands at 1079, 1080 and 1089 together with 1110 cm^{-1} were respectively assigned to $\delta/\pi = 1/4, 1/8$ and $1/12$ for the 4/12, 8/8 and 12/4 acids. Note that *two* lines are observed for the 8/8 acid. These lines arise from a coupling between vibrations of the methyl- and carboxyl-terminated sections which have an equal length in this case. The 1079 cm^{-1} line of the 4/12 acid is strongly influenced by adjacent $\text{C}\equiv\text{C}$ and COOH groups. The 1018 cm^{-1} line for the 4/12 acid might be assigned to $\delta/\pi = 2/4$, but it lies significantly off the dispersion curve. A phase difference of $\delta/\pi = 2/8$ could be attributed to the 1020 cm^{-1} line of the 8/8 acid. No band was observed for the $\delta/\pi = 2/12$ phase difference for the 4/12 acid probably because it overlaps with the very intense 1067 cm^{-1} line.

The frequencies of the methyl-terminated chains are shown in Fig. 7a as right-justified filled symbols (see also Table III). Since the terminal-methyl group is considered to be a free end for a chain vibration, possessing a node at the central acetylene group, the phase differences $\delta/\pi = 1/2m$ and $\delta/\pi =$

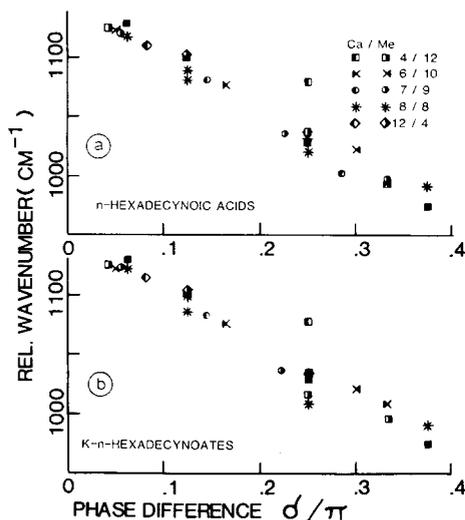


Fig. 7. The phase differences $\delta = k\pi/m$ and $k\pi/n$, for the unsaturated acids: $\text{CH}_3(\text{CH}_2)_m-\text{C}\equiv\text{C}(\text{CH}_2)_n-\text{COOH}$ and the derived potassium-salts are indicated by right-justified, half filled symbols and left-justified ones for the methyl- and carboxyl terminated chains, respectively. * indicates the 8/8 acid and salt, \blacksquare indicate the phase differences for hexadecanoic acid. A phase difference of $\delta = \pi/2m$ was used for the methyl-chain vibration with the highest frequency. See text and Tables III and IV.

TABLE III

ASSIGNMENT OF THE ν_4 -RAMAN BANDS TO SPECIFIC PHASE DIFFERENCES (δ/π) FOR THE *n*-HEXADECYNOIC ACIDS^{a,b}

4/12	6/10	7/9	8/8	12/4
<i>Carboxyl chains</i>				
1079,s(1/4)	1076,s(1/6)	1080,vs(1/7)	1089,vs } (1/8)	1110,vs(1/12)
			1080,vs }	
1018,vw(2/4)	992,vw(2/6)	1002,w(2/7)	1020,w(2/8)	1036,w(3/12)
<i>Methyl chains</i>				
1127,vs(1/24)	1124,vs(1/20)	1121,vs(1/18)	1118,vs(1/16)	1101,s(1/8)
		1036,m(2/9)	1031,w(2/8)	1015,m(2/4)
1036,vw(3/12)	1022,m(3/10)	993,m(3/9)	992,w(3/8)	
993,vw(4/12)				

^aSee text for explanation.

^bAcids are denoted according to the number of carbon atoms in the carboxyl- and the methyl chain, e.g. (ca/me) acid.

TABLE IV

ASSIGNMENT OF THE ν_4 -RAMAN BANDS TO SPECIFIC PHASE DIFFERENCES (δ/π) FOR THE POTASSIUM *n*-HEXADECYNOATES^{a,b}

4/12	6/10	7/9	8/8	12/4
<i>Carboxyl chains</i>				
1077,s(1/4)	1075,w(1/6)	1081,m(1/7)	1098,vw 1085,s	1114,m(1/12) (1/8)
1015,vw(2/4)	1008,vw(2/6)		1007,w(2/8)	1073,w(2/12) 1033,vw(3/12)
<i>Methyl chains</i>				
1126,vs(1/24)	1122,s(1/20)	1123,s(1/18) 1035,w(2/9)	1122,m(1/6) 1032,m(2/8)	1102,s(1/8) 1005,vw(2/4)
1033,w(3/12)	1021,vw(3/10)		990,vw(3/8)	

^aSee text for explanation.

^bSalts are denoted according to the number of carbon atoms in the carboxyl- and the methyl chain, e.g. (ca/me) potassium salt.

k/m , where $k = 2, 3, \dots$, have been used. The 6/10 and 7/9 acids exhibit strong bands at 1124 and 1121 cm^{-1} , which were respectively assigned to $\delta/\pi = 1/20$ and 1/18. The other lines near 1127 (4/12 acid), 1118 (8/8 acid) and 1101 cm^{-1} (12/4 acid) were attributed to $\delta/\pi = 1/24$, 1/16 and 1/8, respectively. Phase differences $\delta/\pi = 2/9$ and 2/8 were assigned to the 1036 (7/9 acid) and the 1031 cm^{-1} (8/8 acid) lines, respectively. No lines could be correlated with the phase differences $\delta/\pi = 2/12$ and 2/10. The 1036 (4/12 acid), 1022 (6/10 acid) and 993 cm^{-1} (7/9 acid) lines were attributed to the phase differences $\delta/\pi = 3/12$, 3/10 and 3/9, respectively and the 992 cm^{-1} (8/8 acid) might be related to $\delta/\pi = 3/8$. A phase difference of $\delta/\pi = 4/12$ could be assigned to the 993 cm^{-1} line of the 4/12 acid. Since it is to be expected that the methyl segment of the 4/12 acid would have similar frequencies to the carboxyl segment of the 12/4 acid, the 1036 cm^{-1} line (12/4 acid) could be assigned to $\delta/\pi = 3/12$. The 1015 cm^{-1} band could be attributed to $\delta/\pi = 2/4$ (12/4 acid) following similar reasoning.

Potassium n-hexadecynoates

The assignment of the ν_4 -Raman bands of the potassium salts was carried out as described above for the acids. The strong fundamental modes with $k = 1$ were easily attributed. The lines belonging to the overtones were weaker compared to the corresponding bands of the acids. Results are shown in Table IV and Fig. 7b. The 1114 cm^{-1} line is probably due to the $\delta/\pi = 1/12$ vibration of the 12/4 potassium salt. This is consistent with the

progression in the intensities of the lines for which $\delta/\pi = 1/6, 1/7$ and $1/8$ (Tables II and IV).

Conclusion

The results presented in Fig. 7 and Tables III and IV show that the dispersion curves for the vibrations of the carboxyl- and methyl-terminated chain segments are in good agreement with that obtained for the saturated acid. This indicates that the introduction of an acetylenic link into the polymethylene chain effectively decouples the skeletal vibrations of the two alkyl segments. Thus a spatial resolution along the chain length has been created which might be utilized in studies of membrane systems by joining perdeuterated and protonated chain segments by an acetylenic bond. This provides a better alternative to the approach of Merajver [26], where saturated, and thus coupled, polymethylene chains have been partially perdeuterated.

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References

- 1 J.L. Lippert and W.L. Peticolas, *Biochim. Biophys. Acta*, 282 (1972) 8.
- 2 Y. Koyama and K.-I. Ikeda, *Chem. Phys. Lipids*, 26 (1980) 149.
- 3 N.W. Gilman and B.C. Holland, *Synth. Commun.*, 4 (1974) 199.
- 4 N.W. Gilman and B.C. Holland, *Chem. Phys. Lipids*, 13 (1974) 239.
- 5 K.C. Eberly, *J. Org. Chem.*, 26 (1961) 1309.
- 6 R.G. Brown, *J. Chem. Phys.*, 38 (1963) 221.
- 7 I.R. Hill and I.W. Levin, *J. Chem. Phys.*, 70 (1979) 842.
- 8 M. Suzuki and T. Shimanouchi, *J. Mol. Spectrosc.*, 29 (1969) 415.
- 9 J.C. Lavalley, J. Saussey and J. Lamotte, *Spectrochim. Acta*, 35A (1979) 695.
- 10 M.J. Murray and F.F. Cleveland, *J. Am. Chem. Soc.*, 63 (1941) 1718.
- 11 F.F. Cleveland, M.J. Murray and H.J. Taufen, *J. Chem. Phys.*, 10 (1942) 172.
- 12 G. Vergoten, G. Fleury and Y. Moschetto, in: R.J.H. Clark and R.E. Hester (Eds.), *Advances in "Infrared and Raman Spectroscopy"*, Vol. 4, Chap. V, Heyden, London, 1978, p. 195.
- 13 R. Faiman and D.A. Long, *J. Raman Spectrosc.*, 3 (1975) 371.
- 14 M. Tasumi, T. Shimanouchi and T. Miyazawa, *J. Mol. Spectrosc.*, 9 (1962) 261.
- 15 J.H. Schachtschneider and R.G. Snijder, *Spectrochim. Acta*, 19 (1963) 117.
- 16 T. Shimanouchi and M. Tasumi, *Indian J. Pure Appl. Phys.*, 9 (1971) 985.
- 17 D.H. Reneker and B. Fanconi, *J. Appl. Phys.*, 46 (1975) 4144.
- 18 J.F. Rabolt, R. Twieg and C. Snijder, *J. Chem. Phys.*, 76 (1982) 1646.
- 19 J.F. Rabolt, *J. Polym. Sci.*, 17 (1979) 1457.

- 20 G. Minoni and G. Zerbi, *J. Phys. Chem.*, 86 (1982) 4791.
- 21 B. Wojtkowiak, *Ann. Chim.*, 9 (1964) 5.
- 22 J. Saussey, J. Lamotte and J.C. Lavalley, *Spectrochim. Acta*, 32A (1976) 763.
- 23 R.G. Snijder, S.L. Hsu and S. Krimm, *Spectrochim. Acta*, 34A (1978) 395.
- 24 R.N. Jones and R.A. Ripley, *Can. J. Chem.*, 42 (1964) 305.
- 25 H. Okabayashi and T. Kitagawa, *J. Phys. Chem.*, 82 (1978) 1830.
- 26 S.D. Merajver, *Chem. Phys. Lipids*, 29 (1981) 379.