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Raman spectroscopic study of allyl methyl ether (3-methoxy-1propene), $CH_2 = CHCH_2OCH_3$, and some isotopically labelled analogues

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Abstract

Fourier-transform Raman spectra of allyl methyl ether, $CH_2 = CHCH_2OCH_3$, three deuterated derivatives and one ¹³C derivative have been obtained. Comparison of the spectra of the deuterated and protiated compounds in conjunction with polarization data has enabled full vibrational assignments to be made for the carbon-hydrogen modes and the ¹³C data have identified some skeletal modes of the CO and CC bonds. As a result of the data obtained from the deuterated compounds in particular, some initial suggestions have been revised for tentative literature assignments of molecules of biological interest. In other cases, confirmation of existing assignments has been made.

1. Introduction

In previous Raman spectroscopic studies in our laboratories, vibrational band assignments of the human keratotic species skin, callus, hair and nail [1], and some complex biopolymers including wool [2] and cotton [3] have been proposed. In several cases, the unequivocal identification of important modes is fraught with difficulty because of the presence of spectroscopic features arising from ν (CH), ν (CO) and ν (CN) vibrations which occur in the same wavenumber regions. For example, in a recent vibrational Raman study of healthy and diseased human stratum corneum [4], some critical spectroscopic differences were noted in the ν (CH). stretching and $\delta(CH_2)$ deformation regions of the spectra; these were ascribed to delipidization

processes which occurred in the epidermal regions of the diseased tissues. Again, in parallel studies [5,6] of the effects of chemical enhancers on transdermal drug delivery using FT-Raman spectroscopy, it was concluded that the influence of enhancing agents such as dimethyl sulphoxide on the ν (CH) bands of human skin occurs via a lipid transmission mechanism in which water is also involved.

A further problem can arise in the vibrational assignment of large molecules when considering small molecular species as templates or models in that the tertiary structures can alter substantially the appearance of the spectra. This phenomenon was experienced in some recent work on celluloses [3] and on bacterial wall cells [7], where molecular assignment comparisons based on glucose or mannose were found to be deficient because of biomolecular rigidity imposed by the β -glycosidic linkages.

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In the current work, a series of isotopically labelled analogues of allyl methyl ether (3-methoxy-1propene), $CH_2 = CHCH_2OCH_3$, in which deuterium substitution has been effected on the O-methyl group and/or in the α -methylene group, has been investigated. A ¹³C-analogue labelled in the O-methyl group has also been studied. Selection of allyl methyl ether as a parent species for the vibrational spectroscopic isotopic study was motivated by the presence of features which also occur in less easily identifiable form in larger molecules of biological interest, such as β -carotene, lipids, cellulose and keratins. The unequivocal identification of ν (CH) and δ (CH₂) modes in all we ther and its isotopically substituted analogues will therefore assist the vibrational spectroscopic identification and assignment of corresponding features in molecules of biological interest.

2. Experimental

2.1. Synthesis of isotopically substituted molecules

The ethers required for this work were synthesized by the routes summarized in Scheme 1 by stirring a suspension of the alkoxide of the requisite allyl alcohol in triglyme (triethylene glycol dimethyl ether, $CH_3O(CH_2CH_2O)_3CH_3$) with a slight deficiency (0.7–0.9 mol) of the appropriate methyl iodide for 18–48 h. The product was isolated by distillation (b.p. 40–44°C), washed with water, dried with magnesium sulphate and redistilled from a small quantity of sodium hydride dispersion to give the desired allyl methyl ether (b.p. 41–42°C) in 30–60% yield.

1. $H_2C=CHCH_2OH \xrightarrow{i,ii} H_2C=CHCH_2OCH_3$

2. $H_2C=CHCH_2OH \xrightarrow{i,ii} H_2C=CHCH_2OCD_3$

3. $H_2C=CHCOCl \xrightarrow{iv,v} H_2C=CHCD_2OH$

 $\xrightarrow{i,ii}$ H₂C=CHCD₂OCH₃

4. $H_2C=CHCD_2OH \xrightarrow{i,iii} H_2C=CHCD_2OCD_3$

5.
$$H_2C = CHCH_2OH \xrightarrow{i, \forall i} H_2C = CHCH_2O^{13}CH_3$$

Reagents and conditions

i, NAH (1.2 mol of 60% dispersion in mineral oil) in triglyme; ii, CH₃I (0.9 mol in triglyme; stir 18–48 h; iii, CD₃I (0.9 mol) in triglyme; stir 18–48 h; iv, addition to LiAlD₄ (0.6 mol in diethyl ether at -45 to -25° C; v, aqueous NaOH solution; vi, ¹³CH₃I (0.9 mol) in triglyme; stir 24 h.

All starting materials, including CD₃I, LiAlD₄ and ¹³CH₃I were high purity samples obtained from Aldrich and were used without further purification. The estimated isotopic purity of the deuterated ethers exceeded 95%; that of the ¹³C-labelled ether was 99%. The general procedure is illustrated by the following detailed description of the synthesis of $[1,1-^{2}H_{2}]$ allyl [²H₃]methyl ether.

2.2. Synthesis of $[1,1^{-2}H_2]$ allyl $[^{2}H_{3}]$ methyl ether, CH₂=CHCD₂OCD₃

$CH_2 = CHCD_2OH$

A suspension of lithium aluminium deuteride (5.0 g, 0.12 mol) in dry diethyl ether (300 cm^3) was stirred magnetically under a nitrogen atmosphere and cooled to -25° C. A solution of acryloyl chloride (19.0 g, 0.21 mol) in dry diethyl ether (60 cm³) was added dropwise over 2.75 h while the reaction temperature was maintained between -25 and -45° C. The stirred reaction mixture was allowed to warm to -5° C; the reaction flask was immersed in a large bowl of ice and stirring was continued overnight. After hydrolysis by cautious dropwise addition of water (5 cm^3), 10% aqueous sodium hydroxide solution (15 cm^3) and water (5 cm^3) , the ethereal phase was filtered at the pump and the inorganic salts were washed with diethyl ether $(3 \times 50 \text{ cm}^3)$. The combined ethereal phases were dried (magnesium sulphate), filtered and distilled through a 10 cm helix-packed column. The bulk (approximately 450 cm³) of the diethyl ether was removed (b.p. 33.5-35°C), the residual material was redried (magnesium sulphate), filtered into a smaller distillation flask and triglyme (40 cm³) was added. Careful distillation through the fractionating column gave an ethereal forerun (b.p. 33.5–35°C), followed by $[1,1-{}^{2}H_{2}]$ allyl alcohol as a pale yellow liquid (5.5 g, b.p. 87-96°C). Redistillation from a

small quantity of sodium hydride (0.2 g of 60% dispersion in mineral oil) gave colourless $[1,1-^{2}H_{2}]$ allyl alcohol (5.5 g, b.p. 93–96°C). This procedure is a modification of an earlier method [8].

$CH_2 = CHCD_2OCD_3$

A solution of $[1,1^{-2}H_2]$ allyl alcohol (0.69 g, 0.0115 mol) in triglyme (15 cm³) was stirred magnetically under a nitrogen atmosphere; sodium hydride (0.75 g of 60% dispersion in mineral oil, 0.19 mol) was added in two portions. After hydrogen evolution had ceased (20 min), a solution of ²H₃-iodomethane (1.45 g, 0.01 mol) in triglyme (2 cm³) was added dropwise over 20 min and stirring was continued overnight. Careful distillation gave the desired ether (0.47 g, b.p. 41–45°C). This material was washed with water (0.5 cm³), dried (magnesium sulphate), filtered and redistilled from a trace of sodium hydride (0.05 g of 60% dispersion in mineral oil) to give



Fig. 1. Molecular structure of allyl methyl ether (3-methoxy-1propene) on the basis of C_8 molecular symmetry.

 $[1,1-{}^{2}H_{2}]$ allyl $[{}^{2}H_{3}]$ methyl ether (0.27 g, 35%, b.p. 41-42°C).

2.3. Raman spectroscopy instrumentation

FT-Raman spectra were recorded using a Bruker FRA106 Raman module on a Bruker IFS66 optics system. An Nd: YAG laser operating at 1064 nm was used as an excitation source and the laser beam was focussed to a spot of 100 μ m diameter at the



Fig. 2. FT-Raman spectrum of allyl methyl ether; $\Delta \tilde{\nu} = 250-3400 \text{ cm}^{-1}$; $\lambda = 1064 \text{ nm}$; 2000 scans; 4 cm⁻¹ spectral resolution.

sample. Samples of the allyl methyl ether and its ²H- and ¹³C-labelled analogues were contained in sealed capillary tubes mounted in a specially constructed holder. Laser powers of up to 500 mW were used with typically 2000 scans at 4 cm⁻¹ spectral resolution being collected. A liquid-nitrogen-cooled germanium detector with extended spectral bandwidth was used over the scan range of $50-3500 \text{ cm}^{-1}$; spectra were corrected for instrument response and the observed band wavenumbers, calibrated against the internal laser frequency, are correct to better than $\pm 1 \text{ cm}^{-1}$. Polarization measurements were made with an optical vector rotator in the laser beam.

3. Vibrational theory

For C_s molecular symmetry, as indicated

diagrammatically in Fig. 1, the vibrational modes may be classified as follows

$$\Gamma_{\rm vib} = 21A' + 12A''$$

all of which are Raman-active and 21 bands will be polarized in the Raman spectrum.

For the penta-atomic skeletal modes only, the following vibrational classification now applies

$$\Gamma_{\rm vib}^{\rm skeletal} = 7A' + 2A''$$

for which there will be seven bands polarized in the Raman spectrum.

4. Results and discussion

The FT-Raman spectrum of unsubstituted allyl methyl ether is shown in Fig. 2. From this spectrum the complexity of the ν (CH) and



Fig. 3. FT-Raman spectra of allyl methyl ethers, with substitution of D and ¹³C isotopes at prescribed groups, conditions as for Fig. 2; $\Delta \tilde{\nu} = 2600-3400 \text{ cm}^{-1}$; (a) CH₂=CHCD₂OCD₃; (b) CH₂=CHCD₂OCH₃; (c) CH₂=CHCH₂OCD₃; (d) CH₂=CHCH₂OCH₃; (e) CH₂=CHCH₂O¹³CH₃.

 δ (CH₂) skeletal regions indicates the problem faced in molecular vibrational assignments for even an apparently simpler case. However, by substitution of deuterium for protium in the O-methyl group and on the α -C atom to the ether linkage, the identification of CH₂ and CH₃ modes is simplified. The isotopically labelled materials utilized for this task are CH₂=CHCH₂OCD₃, CH₂=CHCD₂OCH₃, CH₂=CHCD₂OCD₃ and also CH₂=CHCH₂O¹³CH₃, which was included in an attempt to assign the skeletal modes arising from ν (CO) and ν (CC) vibrations with more confidence.

Stack plots of the FT-Raman spectra of the ²Hand ¹³C-labelled molecular species, and the unsubstituted materials for comparison purposes, are shown in Figs. 3, 4 and 5 for the wavenumber regions 3400–2600, 2400–1800 and 1800–250 cm⁻¹, which represents ν (CH) stretching, ν (CD) stretching and ν (CC), ν (CO), δ (CH₂) skeletal and deformation regions, respectively. For simplicity, the polarized and depolarized components are not shown in the figures.

The wavenumbers and relative intensities of the vibrational bands are given in Table 1.

We shall now consider each wavenumber region:

4.1. $3400-2600 \text{ cm}^{-1}$

This is the region where ν (CH) and ν (CD) stretching are expected [9]. From group theoretical considerations we should expect to observe eight bands in the Raman spectrum, of which six are polarized in the ν (CH) stretching region and their wavenumbers and polarizations are indicated in Table 1. Comparison of the observed spectra in this region with those of the ν (CD) stretching region has enabled the unequivocal assignment of the molecular features to be made for the first time in this type of molecule. Effectively, it has now



Fig. 4. Conditions and spectra as for Fig. 3 but wavenumber range 2500-1800 cm⁻¹.

Table 1 Wavenumber (cm ⁻¹), po	larization data and propos	ed vibrational assignments f	or allyl methyl ether and isc	otopically labelled analogues	
CH ₂ =CHCD ₂ OCD ₃	CH ₂ =HCD ₂ OCH ₃	CH ₂ =CHCH ₂ OCD ₃	CH ₂ =CHCH ₂ OCH ₃	CH ₂ =CHCH ₂ O ¹³ CH ₃	Approximate assignment of vibrational mode
3084 m.pol.	3084 m,pol.	3804 m,pol.	3804 m,pol	3804 m,pol	v(CH)
3017 <i>iie</i> nol	3017 ve nol	3017 vs nol	3017 ve aol	3044 vw 3017 201	(1647 + 1451) = 3098
2017 vs.put. 2985 s.nol.	2985 s.nol.	2985 s.pol.	2985 s.nol.	2985 s.nol.	$\nu(CH_5=C)$ asymmetric $\nu(CH_5=C)$ symmetric
	2935 m,pol.	In Jacobs	2938 m.pol.	2935 m,pol.	$\nu(CH_3)$ asymmetric
	•	2919 mw	2919 mw	2919 mw	$\nu(CH_2)$ asymmetric
	2892 m		2892 m	2887 m	$\nu(\mathrm{CH}_3)$ asymmetric
		2848 m,pol	2848 m,pol.	2848 m.pol	$\nu(\mathrm{CH}_2)$ symmetric
		2836 mw			(1648 + 1288) = 2936
		1626	2822 s.pol.	2818 s.pol.	$\nu(CH_3)$ symmetric
110 Mar 100	MA 06/7	MA 16/7	MA 1617	MA 06/7	$(1400 \pm 1200) = 2/48$ $(874 \pm 1415) = 7980$
2239 vw	2238 vw	2240 vw	I		$(819 \pm 1415) = 2234$
2191 mw br nol		2191 mw hr nol			$v(\mathbf{CD}_{i})$ asymmetric
2130 m.denol.	2130 m.denol.				$\nu(CD_2)$ asymmetric
2109 mw.depol.		2109 mw,depol			$\nu(CD_3)$ asymmetric
2076 m.shpol.	2076 s.br.,pol.	• `			$\nu(CH_2)$ asymmetric
2058 s.pol.	T	2058 s.pol.			$\nu(CD_3)$ asymmetric
T,	2041 vw	T,			(1640 + 405) = 2045
1645 s,pol.		1648 s,pol.	1648 s,pol.	1647 s,pol.	$\nu(C=C)$
1640 m.sh.	1640 s,pol		1	I	
1618 w	1618 w	1618 w	1618 w	1618 w	
	1462 m,sh.	1460 m,sh.	1460 w	1467 w	δCH_2 scissors
	1451 m,pol.		1451 m.pol.	1451 m,pol.	$\delta(\mathrm{CH_3})$
		1427 mw	1424 mw	1424 mw	$\delta(CH_3)$ asymmetric
1415 ms,depol.	1415 ms, depol.	1413 mw,depol.	1411 w	1411 w	$\delta(\mathrm{CH}_2), \delta(\mathrm{CH}_3)$
		1365 w	1359 w	1323 m	$\delta(CH_3)$ symmetric
1291 s,pol.	1291 s,pol.	1288 s,pol.	1288 s,pol.	1286 s,pol.	$\delta(CH)$ twist
		1242 mw	1247 w	1243 w	$\delta(\mathrm{CH}_2)$
1192 w				1190 w	
1148 vw				1148 mw	
1133 m				1133 m	
1112 w			1112 w		u(COC) allyl out-of-phase
	1098 mw	1098 mw			ν (COC) allyl out-of-phase
			1085 w		
1066 m	1066 m				v(CC)
1054 m		1054 m		1020	$\delta(CD_3)$
1018 mw	1014 w	1014 w		w 2001	k(CD,)· &(CD,)
	995 mw		995 w	995 w	u(~~3); u(~~1)

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ν(CO)	v(CC)	p(CH ₃)	v(COC)	ν (COC); ρ (CH ₃) in-phase		v(CCO)	v(CO)	~		δ(C=CH) in-plane wag	$\delta(COCH_1); \delta(COCD_1)$	é(coc)	6(CCO); 6(COC)	6(COC); 6(CCO)	w(crcn)
974 mw 961 mw	920 m	913 mw		895 s,pol.	870 mw		853 mw		819 w		493 mw	417 m		388 w	340 w
974 mw	928 mw,sh.,pol. 920 mw	913 mw	901 ms,pol.		874 mw							422 m			
	928 mw,sh,pol. 922 mw			895 vw		857 ms	846 mw		819 w				504 m		
	928 s,pol.	913 mw			874 s	857 ms	846 mw	828 m	819 w	602 mw	518 mw		405 m	374 m	
	928 w,pol.				874 ms		846 mw	828 mw	819 ms	602 mw	518 mw		399 m		357 m



Fig. 5. Conditions and spectra as for Fig. 4 but wavenumber range $1800-250 \text{ cm}^{-1}$.

been made possible to ascribe wavenumbers to the $\nu(CH_2=C)$, $\nu(CH=C)$, $\nu(CH_2)$ and $\nu(CH_3)$ modes of this species.

Hence, the medium intensity, polarized band at 3084 cm^{-1} , which occurs in all samples studied, is assignable to the ν (CH) in-plane stretching vibration. The strong, polarized bands at 3017 and 2985 cm^{-1} also occur in all spectra and are assigned to the $\nu(CH_2=C)$ asymmetric and symmetric in-plane stretching vibrations, respectively. For this grouping, since the $CH_2 = C$ group is shown in the σ plane of the molecule (Fig. 1), the presence of two polarized bands for the $\nu(CH_2=C)$ stretching modes confirms the C_s molecular symmetry. These three modes are all expected for the CH₂=CH- vinyl end-groups of the ethers studied; all other ν (CH) modes for the CH₂ and CH₃ groups bound to the oxygen atom are locatable through the deuterium substitutions carried out in this study. Hence, the five remaining ν (CH) modes of the CH₂, CH₃ groups now expected in the 2800-3000 cm⁻¹

region will move to the $2000-2200 \text{ cm}^{-1}$ region on substitution of D for H.

Thus, the $\nu(CH_3)$ asymmetric stretch (polarized) at about 2935 cm⁻¹ moves to 2191 cm⁻¹ in the -CD₃ compounds, CH₂=CHCD₂OCD₃ and CH₂=CHCH₂OCD₃, but is absent in this wavenumber region for CH₂=CHCD₂OCH₃ and CH₂=CHCH₂OCH₃. The isotopic ratios of $\nu^{\rm H}$ to $\nu^{\rm D}$ for the CH₂ and CH₃ bands range between 1.34 and 1.37. Similarly, the $\nu(CH_2)$ and $\nu(CH_3)$ symmetric stretches at 2848 and 2822 cm⁻¹ move to 2076 and 2058 cm⁻¹, respectively, on deuteration. Other very weak features in the $\nu(CH)$ and $\nu(CD)$ stretching regions at 3044, 2730 and 2240, 2041 cm⁻¹ are assignable to combination bands of fundamental skeletal modes.

4.2. $1800-250 \text{ cm}^{-1}$

In this wavenumber region we expect [9] to observe the nine predicted skeletal stretching and

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deformation modes (seven polarized), including ν (C=C), ν (C-C) and ν (C-O) features. It is realised that fundamentally the deuterium substitution should not affect the wavenumbers of these skeletal modes, but in practice small observed wavenumber shifts may be ascribed to the influence of mode mixing, primarily with deformations of the CH₂ and CH₃ groups in the same symmetry classes. The ¹³C-substitution of the O-methyl group carbon atom should be of use in the identification of the $\nu(CO)$ mode belonging to this species, but small shifts in other modes might again be expected from contributions of the ν (CO). In this region, therefore, in addition to the nine modes expected for the C=CCOC skeleton, 16 modes (8A' and 8A'') will be expected for CH, CH₂ and CH₃ motion. These will consist of deformations of the type $\delta(CH_2)$, $\delta(CCH)$, $\delta(CH_3)$ and rocking or wagging modes of the type $\rho(CH_2)$, $\rho(CH_3)$, $\rho(CCH)$. Some important assignments for this region will now be discussed.

The $\nu(C=C)$ stretching vibration is seen at $1640-1648 \text{ cm}^{-1}$, polarized; the variation of wavenumbers with deuteration here is a little surprising since the deuterium atoms are not directly attached to the C=C linkage; however, the α -CD₂ unit seems to have a significant effect on the $\nu(C=C)$ vibration, since for both $CH_2 = CHCD_2OCH_3$ and CH₂=CHCD₂OCD₃ there are features at 1640 cm^{-1} compared with that at 1648 cm^{-1} for $CH_2 = CHCH_2COCH_3$. It is interesting that for the $CH_2 = CHCD_2COCD_3$ compound the strong feature ascribed to ν (C=C) at 1645 cm⁻¹ has a shoulder at 1640 cm^{-1} , which presumably results from the influence of deuterium substitution at both the α -CH₂ and terminal methyl groups.

In the 1470–1200 cm⁻¹ region, the CH₂=CHCH₂ and CH₃ deformations are expected [9]; again, as found for the ν (CH) stretching region, the deuteration of the CH₂ and CH₃ groups and polarization data assist materially the assignment of the observed bands.

Hence, the bands in the region $1410-1470 \text{ cm}^{-1}$ are assigned to $\delta(\text{CH}_2)$ and $\delta(\text{CH}_3)$ vibrations; these would be expected to occur around $1000-1050 \text{ cm}^{-1}$ for the deuterated species. Likewise, the rocking vibrations around 900–950 cm⁻¹ for

the CH_2 and CH_3 groups are expected to occur near 640–680 cm⁻¹ for the deuterated compounds.

Generally, it is possible to assign reasonable descriptions for the vibrational modes in the skeletal region, bearing in mind that in many cases combinations of modes may be represented by a single observed wavenumber. For example, the lower frequency modes in the $300-600 \text{ cm}^{-1}$ region are probably combinations of δ (CCO), δ (COC) and δ (C=CH) deformations [9]. Hence, the listing of the modes in Table 1 for skeletal vibrations, which may be subject to CH₂ and CH₃ mode mixing, will often be revealed by small changes in wavenumber on deuteration of the CH₂ and CH₃ groups, such as the band at 1291 cm⁻¹, which is formally described as a δ (CH) twisting mode, and the $\delta(COC)$ out-of-phase vibrations at 1112 and 1098 $\rm cm^{-1}$.

The substitution of ¹³C in the O-methyl group has not produced the more obvious effects produced by deuteration on the CH₂ and terminal CD₃ groups. However, small changes in wavenumber of the skeletal COC modes are to be expected, e.g. 518 to 493 cm⁻¹ for δ (COCH₃), 901 to 895 cm⁻¹ for ν (COC) and 422 to 417 cm⁻¹ for δ (COC) modes from a comparison between the spectra of the CH₂=CHCH₂COCH₃ and CH₂=CHCH₂O¹³CH₃ species.

5. Conclusions

The conclusions of this study are sometimes a little surprising and demonstrate the value of isotopic substitution (particularly D for H) especially in the CH₃ and CH₂ stretching bending and rocking regions of the spectrum. The combined polarization and deuteration data clearly confirm the assignment of the 2848 cm⁻¹ band to a ν (CH₂) symmetric stretch, which has been tentatively proposed in the literature [1,9]. However, the 2892/2887 cm⁻¹ mode is clearly a ν (CH₃) asymmetric mode and this has formerly been ascribed [1,9] to $\nu(CH_2)$ symmetric stretching. Likewise, the 2730 cm⁻¹ combination band, previously assigned to a ν (CH) aliphatic mode [1,9], also cannot be of this description as it is present in deuterated molecules; the ν (CH) mode is more properly assigned to the 3084 cm⁻¹ band. Similarly, a band at 1450 cm⁻¹ in keratotic tissue [1], previously assigned on a literature basis [9] to a $\delta(CH_2)$ scissors mode, is better reassigned to a $\delta(CH_3)$ vibration on the basis of this deuterium labelling study. The $\delta(CH)$ twisting mode at 1291–1286 cm⁻¹ here clearly cannot be a $\delta(CH_2)$ mode, to which it has been ascribed in biological tissues [9], because it also occurs as a strong, polarized band in $-CD_2$ - species.

The band at 928 cm⁻¹ observed here and assigned to a ν (CC) vibrational mode has previously been suggested to be a ρ (CH₃) terminal methyl mode. Since it is also present in the $-CD_3$ species this cannot be so and our revised assignment better fits the case study. Conversely, a band at 883/891 cm⁻¹ observed in biological specimens and ascribed to a ρ (CH₂) rocking mode is shown to be properly assigned.

We propose to extend this study to other series of simple organic molecules which are building units for larger biological molecules, particularly those deuterated in prescribed positions, to investigate systematically the correctness of the proposed assignments and thereby assist the elucidation of chemical processes such as the role of enhancers in dry delivery systems.

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