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## Infrared spectra of crystalline methyl alkanoates

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**Abstract**—Infrared spectra from 650 to 1350  $\text{cm}^{-1}$  of crystalline homologous methyl esters from methyl propionate to methyl stearate have been observed. Prominent bands of methyl propionate are assigned to fundamental modes assuming  $C_s$  symmetry. A basis is suggested for the well known observation that methyl esters exhibit a characteristic triplet in the 1200  $\text{cm}^{-1}$  region. The assignment of methyl propionate is taken as a starting point for evaluation of the spectra of higher homologues, which are qualitatively interpreted in terms of vibrational coupling between group frequencies. Spectral changes produced by unsaturation are briefly discussed and analytical applications evaluated.

THE infrared spectra of crystalline carboxylic acids have been studied by numerous investigators [1-5]. In recent years it has become important to study the spectra of carboxylic acids in the form of their methyl esters, because separation techniques such as gas-liquid chromatography are most conveniently applied to methyl-esterified samples. The methyl esters of normal saturated carboxylic acids up to a chain length of  $\text{C}_{16}$  melt close to or below room temperature. Branching and unsaturation tend to lower the melting point further. In the liquid state or in solution molecules containing long  $(\text{CH}_2)_n$  chains exhibit profound rotational isomerism and give rise to broad clusters of unresolved absorption bands which are not suitable for characterization of closely related compounds such as members of a homologous series [6].

This communication discusses the infrared spectra of saturated unbranched methyl esters from methyl propionate to methyl stearate, as obtained at temperatures well below the melting points of the compounds.

### EXPERIMENTAL

The esters were gas-chromatographically purified commercial samples. The chromatographic data indicated that the amount of homologous impurities in the final specimens did not exceed a few p.p.m. A low-temperature cell of well known

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- [1] D. HADŽI and N. SHEPPARD, *Proc. Roy. Soc. A* **216**, 247 (1953).
- [2] R. G. SINCLAIR, A. F. MCKAY and R. N. JONES, *J. Amer. Chem. Soc.* **74**, 2570 (1952).
- [3] R. G. SINCLAIR, A. F. MCKAY, G. S. MYERS and R. N. JONES, *J. Amer. Chem. Soc.* **74**, 2578 (1952).
- [4] P. J. CORISH and W. H. T. DAVISON, *J. Chem. Soc.* 2431 (1955).
- [5] H. SUSI, *J. Amer. Chem. Soc.* **81**, 1535 (1959).
- [6] J. K. BROWN, N. SHEPPARD and DELIA M. SIMPSON, *Phil. Trans. A* **247**, 35 (1954).

design [7], cooled with liquid nitrogen, was used. The lower melting esters were sublimed *in vacuo* to a sodium chloride window, the higher ones frozen as thin films between two windows. The spectra were obtained with a Perkin-Elmer Model-21 instrument\* equipped with a sodium chloride prism. Sample thickness could not be determined with any degree of accuracy. Comparison with KBr pellet spectra of approximately known concentration led to an estimated average thickness of the order of 0.01 mm. The samples were not completely randomly oriented, consecutive experiments producing variations in relative intensities of the observed bands. Repeated crystallization from the melt always appeared to result in the same crystal modification. The spectrum of the highest member of the series, methyl stearate, was studied at various temperatures from ca. 15°C below the melting point to liquid nitrogen temperature. No phase change was indicated, although lower temperatures resulted in somewhat sharper absorption bands. The amount of sample used was 2–5 mg. If part of the radiation beam was masked off, reasonably good data could be obtained with a sample of 0.25 mg. This amount could, if necessary, be further decreased by using a beam condensing device in conjunction with a low-temperature cell.

#### RESULTS AND DISCUSSION

The discussion will be limited to the wavelength region between 650 and 1350  $\text{cm}^{-1}$ , i.e. the part of the spectrum where greatest differences are expected for closely related chain molecules [6]. Above 1350  $\text{cm}^{-1}$  CH stretching and bending modes, and the C=O stretching mode are observed. These are essentially "internal" modes of the groups involved and change but little from one homologue to another [6, 9, 10]. In the 1350–650  $\text{cm}^{-1}$  region  $\text{CH}_2$  modes of rotatory origin ("wagging," "twisting," "rocking") are expected [6], together with skeletal vibrations involving C—C and C—O stretching [6, 9, 10], and bending of the OCO angle [10]. Interpretation of the spectra is based on the work of BROWN *et al.* [6] and the work of SNYDER [8] on the infrared and Raman spectra of the n-paraffins, and on the vibrational assignment for methyl acetate by WILMSHURST [10]. Methyl acetate has a planar *cis* structure (point group  $C_s$ ) [10]. The longer homologues in the stable crystalline form probably have an essentially planar zig-zag structure [11] analogous to crystalline hydrocarbons [6] and carboxylic acids [12].

##### *Methyl propionate*

Methyl propionate is the shortest member of the series which contains all groups present in the higher homologues. A reasonable assignment of the bands observed in the region of interest would therefore furnish a logical starting point

\* Mention of commercial products does not constitute an endorsement by the U.S. Department of Agriculture over others of a similar nature not mentioned.

[7] E. L. WAGNER and D. F. HORNIG, *J. Chem. Phys.* **18**, 296 (1950).

[8] R. G. SNYDER, *J. Mol. Spectrosc.* **4**, 411 (1960).

[9] L. J. BELLAMY, *The Infrared Spectra of Complex Molecules*. John Wiley, New York (1958).

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

[11] T. MALKIN, *Progress in the Chemistry of Fats and Other Lipids* Vol. I. (Edited by R. T. HOLMAN, W. D. LUNDBERG and T. MALKIN). Academic Press, New York (1952).

[12] E. v. SYDOW, *Ark. Kem.* **9**, 231 (1956).

for the discussion of the spectra of the whole series. Fig. 1 shows the spectrum of methyl propionate in  $\text{CS}_2$  solution and as a crystalline film. Comparison of the solution spectrum with the spectrum of the solid material indicates that in the propionate rotational isomerism does not yet interfere with a straightforward interpretation in terms of molecular fundamentals. The splittings which are

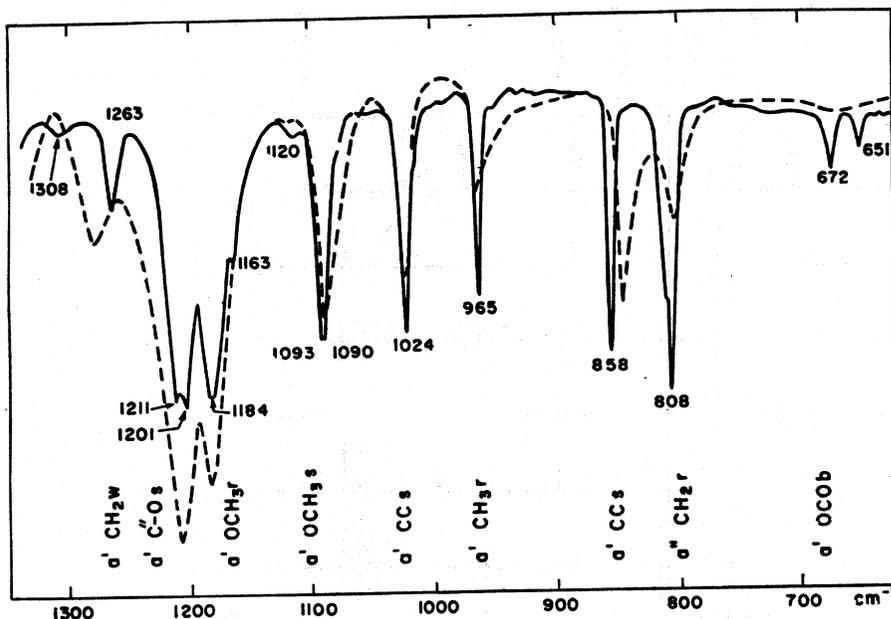


Fig. 1. Absorption spectrum of methyl propionate. Solid line: crystalline film. Dashed line: solution in  $\text{CS}_2$ . s. b. r. w. t: stretching, bending, rocking, wagging, twisting.

present only in the solid spectrum are of a magnitude expected from intermolecular forces in crystals and do not indicate presence of more than one polymorphic form. The assignment, based on  $C_s$  symmetry, is indicated in Fig. 1 and related to methyl acetate on one hand and the higher homologues on the other in Figs. 2 and 3. The assignment between 650 and 1100  $\text{cm}^{-1}$  follows directly from comparison with methyl acetate. Two new bands are easily assigned to the second  $a'$  CC stretching mode and the  $a''$   $\text{CH}_2$  rocking mode. Around 1200  $\text{cm}^{-1}$  three medium to strong bands are observed, assigned to  $a'$   $\text{CH}_2$  wagging,  $a'$   $\text{C}=\text{O}$  stretching and  $a'$   $\text{OCH}_3$

rocking. These three modes, involving stretching of the  $\text{C}=\text{O}$  bond and in-plane rocking of two nearest-neighbor groups are probably strongly coupled. A characteristic triplet results which retains its general form throughout the series of liquid or solution spectra of a great number of aliphatic methyl esters, as observed by SHREVE *et al.* [13] and SINCLAIR *et al.* [2]. Three  $a''$  modes ( $\text{CH}_3$  rock,  $\text{OCH}_3$  rock,

[13] O. D. SHREVE, M. R. HEETHER, H. B. KNIGHT and D. SWERN, *Analyt. Chem.* **22**, 1498 (1950).

CH<sub>2</sub> twist) which are also expected in this region [6, 10] cannot be reliably assigned, although weak unassigned bands are observed at 1308, 1163 and 1120 cm<sup>-1</sup> in the spectrum of the solid material. The *a''* CH<sub>3</sub> rocking modes are very weak in methyl acetate [10]. The CH<sub>2</sub> twisting mode is infrared inactive in propane. In larger

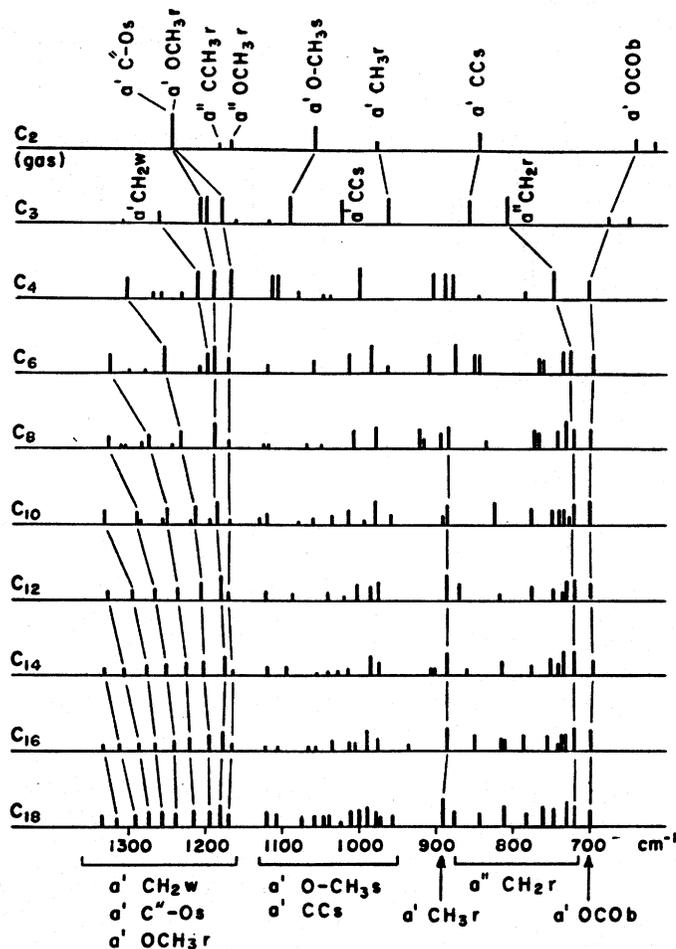


Fig. 2. Schematic presentation of spectra of even-numbered esters as related to methyl propionate.

(even) hydrocarbons the twisting modes are very weak [6]. They become inactive again as the chain length approaches infinity (aside from activity caused by intermolecular forces). Contrary to the in-plane modes of rotatory origin, the out-of-plane modes cannot borrow intensity by mixing with vibrations of the highly polar ester group, because no *a''* ester group modes occur in this region.

The proposed assignment of in-plane modes and the CH<sub>2</sub> rocking mode is in good agreement with propane [6] and, as indicated in Fig. 2, with methyl acetate [10].

### Higher homologues

Fig. 2 presents schematic spectra of all even members and Fig. 3 of all odd members of the series, as related to the proposed assignment of the spectrum of methyl propionate. The two sets of data are presented separately because this facilitates pointing out some inherent regularities. Fig. 4 shows the spectra of two typical adjacent members in some detail.

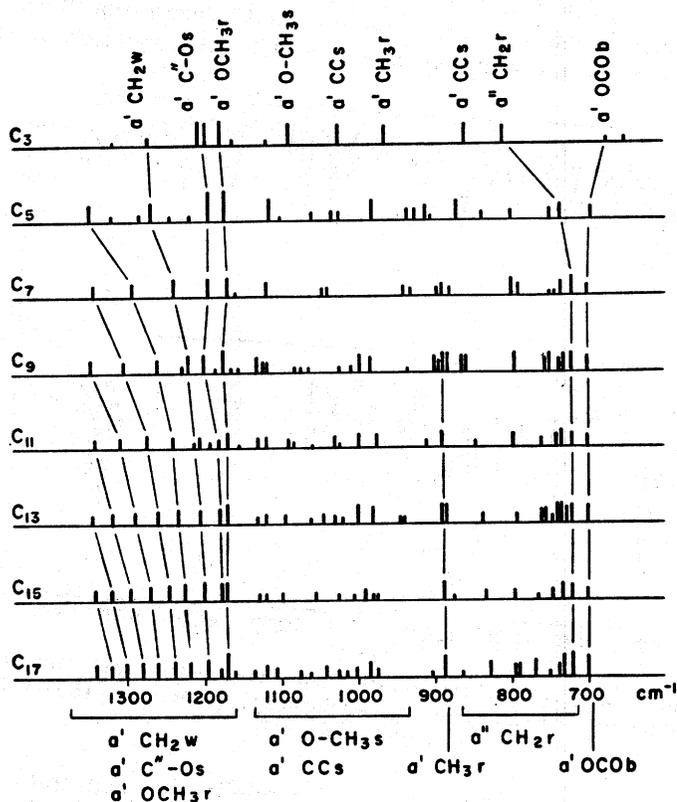


Fig. 3. Schematic presentation of spectra of odd-numbered esters.

If  $n$  is the number of carbon atoms in the acyl part of the molecules,  $n - 1$   $a'$  CC modes and  $n - 2$   $a'$  CH<sub>2</sub> wagging,  $a''$  CH<sub>2</sub> twisting and  $a''$  CH<sub>2</sub> rocking modes are expected in the studied region [6]. Modes with the same symmetry are expected to couple with each other and with ester group vibrations of proper symmetry.  $a''$  CH<sub>2</sub> twisting and  $a''$  CH<sub>3</sub> rocking modes are expected to be inherently weak (cf. previous section). Contrary to *n*-paraffins [6] all fundamentals are infrared and Raman active, selection rules being of no help in classifying the observed bands. Because of this, and the large number of bands expected, it appears futile to discuss all observed bands of the higher homologues in detail. Obvious regularities are discussed below.

In the 1160–1350 cm<sup>-1</sup> region a regular series of bands is observed, which by

comparison with methyl propionate must arise from coupled  $a'$   $\text{CH}_2$  wagging,  $a'$   $\text{C}=\text{O}$  stretching and  $a'$   $\text{OCH}_3$  rocking motions. For the higher even members (from  $\text{C}_{12}$  on) the number of bands corresponds to wagging modes expected from a  $(\text{CH}_2)_{n-2}$  chain ( $n$  even) with  $C_{2h}$  symmetry, plus two ester-group modes ( $\text{C}=\text{O}$  str,  $\text{OCH}_3$  rock.) The series is similar to the one observed in corresponding acids [2-5] where wagging vibrations are coupled with a  $\text{COOH}$  deformation mode in the

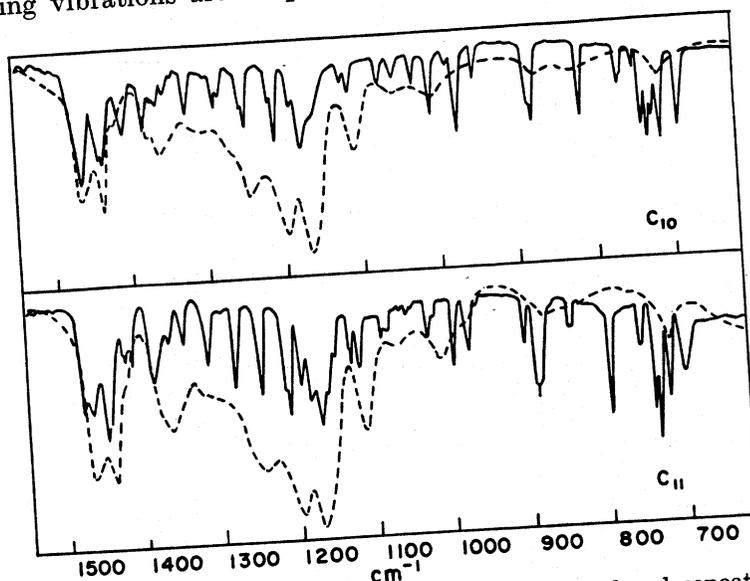


Fig. 4. Absorption spectra of methyl decanoate and methyl undecanoate. Solid line: crystalline film. Dashed line: dilute solution (Solvent:  $\text{CCl}_4$  1500-1000  $\text{cm}^{-1}$ ;  $\text{CS}_2$  1000-650  $\text{cm}^{-1}$ ).

1300  $\text{cm}^{-1}$  region. The bands furnish a nice qualitative example of vibrational coupling of group frequency modes in large molecules [14]. The connecting lines in Figs. 2 and 3 are somewhat arbitrary and merely serve to point out the observed regularities.

Between ca. 850 and 1150  $\text{cm}^{-1}$  ( $n - 1$ )  $a'$   $\text{CC}$  modes coupled with the  $a'$   $\text{H}_3\text{C}-\text{O}$  stretching and  $a'$   $\text{CH}_3$  rocking vibration are expected, resulting in  $n + 1$  fundamentals (nineteen for methyl stearate) crowded into a span of about 300 wavenumber units. Few obvious regularities are apparent, except for a strong, stable band around 900  $\text{cm}^{-1}$  traceable to the 858  $\text{cm}^{-1}$  or the 965  $\text{cm}^{-1}$  fundamental of methyl propionate. A very stable band in this region has been assigned to the methyl rocking mode in long-chain hydrocarbons by SNYDER [8]. The upper limit of the series leads smoothly to the  $a'$   $\text{O}-\text{CH}_3$  str. fundamental of the propionate.

At the low-frequency end of the spectra two bands occur throughout the series around 700  $\text{cm}^{-1}$  and 720  $\text{cm}^{-1}$ . These are easily associated with the  $a'$   $\text{OCC}$

[14] R. C. LORD, F. A. MILLER, *Appl. Spectrosc.* **10**, 115 (1956).

deformation vibration [10] and the limiting  $a''$   $\text{CH}_2$  rocking mode (where all  $\text{CH}_2$  groups move in phase) [6]. The remaining  $n - 3$   $\text{CH}_2$  rocking frequencies most probably account for the remaining bands between 700 and 950  $\text{cm}^{-1}$  (except the stable 890  $\text{cm}^{-1}$  band), but no analyses analogous to n-paraffins [6, 8] is possible because selection rules do not apply. The situation is further complicated by splittings caused by intermolecular forces which in the case of rocking fundamentals of  $-\text{CH}_2-$  chains can be of the order of 10  $\text{cm}^{-1}$  [15].

For the heavier homologues the coupled fundamentals are grouped into

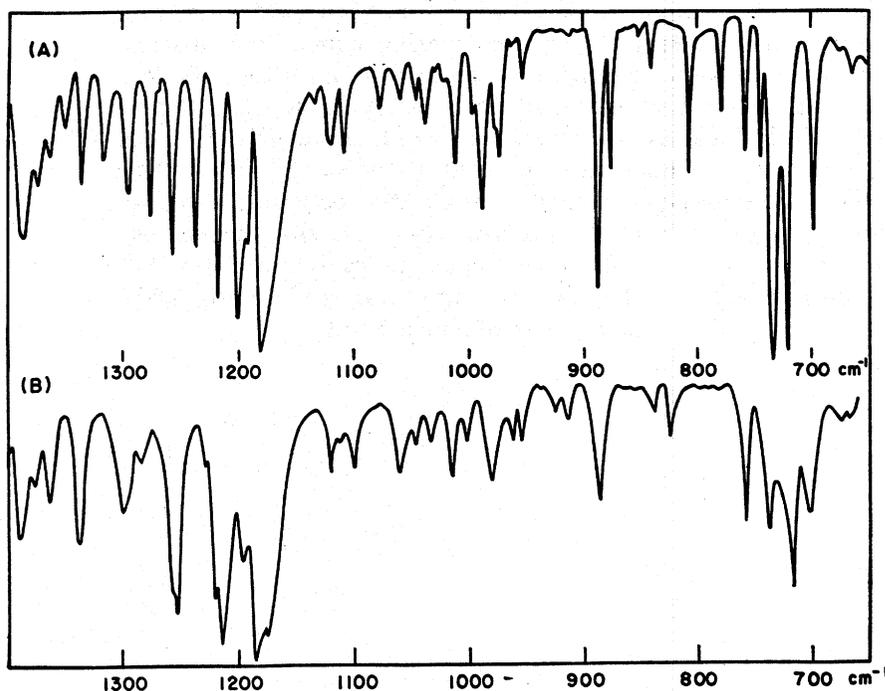


Fig. 5. Absorption spectra of crystalline methyl stearate (A) and methyl linoleate (B).

essentially three clusters of bands, as indicated at the bottom of Figs. 2 and 3. The motions essentially involved in each group of bands, derived from the assignment for methyl propionate, are also indicated.

#### *Unsaturation*

Multiple carbon to carbon bonds interrupt the coupling between  $\text{CH}_2$  units and therefore modify the spectra throughout, as illustrated in Fig. 5 on the example of methyl linoleate. The uncoupling of  $\text{CH}_2$  modes is particularly obvious in the 1150–1350  $\text{cm}^{-1}$  region. In methyl linoleate the number of  $\text{CH}_2$  units attached to the ester grouping by a chain of single bonds is cut approximately in half, and so

[15] R. S. STEIN and G. B. B. M. SUTHERLAND, *J. Chem. Phys.* **22**, 1993 (1954).

is the number of medium strength bands in the above region. The three clusters of bands noted in saturated esters are still recognizable but the number and position of the individual bands has changed. Similar effects have been observed on unsaturated fatty acids [2, 3]. Preliminary experiments have shown that closely related isomeric unsaturated esters exhibit spectra which differ considerably from isomer to isomer.

#### *Analytical application*

Interpretation of the presented data is admittedly far from complete, but the results indicate that certain advantages can be gained by observing the spectra of long-chain methyl esters at temperatures below the freezing point. The spectra, for obvious reasons, are not suitable for quantitative analysis of mixtures. Recent developments of analytical separation methods have rendered a quantitative separation of aliphatic methyl esters an attainable—and frequently not too difficult—process. The emphasis of analytical infrared spectroscopy is therefore on identification. In the case of spectra obtained on solid films polymorphism and irreproducible relative intensities are chief disadvantages. In the case of the investigated pure samples, crystallized from the melt, no polymorphism was observed. Relative intensities are not of paramount importance if identification can be based on the frequencies of a large number of sharp bands.