On the Assignment of a Band at 727 cm^{-1} in Polyethylene Terephthalate

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Some controversy surrounds the assignment of a strong band at 727 cm^{-1} in polyethylene terephthalate. It was first assigned to a C–O–C bending mode1). This assignment is now believed to be incorrect2,3) because it seems much too high for a C–O–C bending mode. The most generally favored explanation is that the band arises from an aromatic C–H out-of-plane bending mode4–6) and therefore that it is similar in origin to a band at 875 cm^{-1}. The removal of the band in question, on going from polyethylene terephthalate to polyethylene deuteroterephthalate2,5), has been considered as strong evidence for this explanation. On the other hand, the present author has proposed an alternative interpretation that two bands at

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1) R. G. J. Miller and H. A. Willis, *Trans. Faraday Soc.*, **49**, 433 (1953).

2) D. Grime and I. M. Ward, ibid., **54**, 959 (1958).

3) A. Miyake, *J. Polymer Sci.*, **38**, 497 (1959).

4) C. Y. Liang and S. Krimm, *J. Chem. Phys.*, **27**, 327 (1957).

5) W. W. Daniels and R. E. Kitson, *J. Polymer Sci.*, **33**, 161 (1958).

6) M. C. Tobin, *J. Phys. Chem.*, **61**, 1392 (954).

875 cm^{-1} and 727 cm^{-1} arise from coupled C-H out-of-plane bending and CO_2 out-of-plane bending vibrations[3].

This problem is of interest because the band mentioned above is in close relation with the so-called extra-bands[7] present in aromatic acids, esters, amides and nitro compounds, the origin of which has yet been unexplained. In order to ascertain whether the author's interpretation is correct or not, some additional observations have been carried out, infrared investigations of polyethylene terephthalate below NaCl region and examinations of thiol esters as model compounds.

Experimental

Material. — 1) *Polyethylene Terephthalate, Polyethylene-d_4 Terephthalate.*—The film samples used are the same as those used in previous researches[3,8].

2) *1,2-Ethanedithiol Dibenzoate.* — Benzoyl chloride (20 g.) was added dropwise with agitation to an ice-cooled solution of 1,2-ethanedithiol (7.5 g.) in pyridine (40 g.). The reaction mixture was allowed to stand overnight and poured into cold dilute sulfuric acid. The solid resulted was collected by filtration and washed successively with aqueous sodium carbonate and water. Repeated recrystallization from ethanol gave white crystals, m. p. 94.5°.

Found: C, 63.18; H, 4.61; O, 10.72. Calcd. for $C_{16}H_{14}O_2S_2$: C, 63.59; H, 4.64; O, 10.59%.

3) *1,2-Ethanedithiol Bis-(4-methoxycarbonylbenzoate).* — A solution of 4-methoxycarbonylbenzoyl chloride (10 g.) in chloroform (50 ml.) was added dropwise with agitation to an ice-cooled solution of 1,2-ethanedithiol (3 g.) in pyridine (40 g.). The reaction mixture, after standing overnight, was poured into cold dilute sulfuric acid with stirring. The solid product obtained as a suspension in the chloroform layer was recrystallized after the addition of ethanol. The resulting crystals were collected by filtration and washed with aqueous sodium hydroxide. Recrystallization from a mixture of ethanol and benzene (1 : 2) gave white crystals, m. p. 208~210°.

Found: C, 57.20; H, 4.35; O, 22.68. Calcd. for $C_{20}H_{18}O_6S_2$: C, 57.40; H, 4.33; O, 22.94%.

Infrared Spectra*. — The infrared spectra were obtained by means of Perkin-Elmer spectrometers model 21, 13 and 321 with NaCl, KBr and CsBr prisms respecively.

The polymer films were investigated in the KBr and CsBr regions. The two thiol esters were investigated in the NaCl and KBr regions as Nujol mulls and KBr disks. Dichroic measurements for the polymer were made in the KBr region on drawn films. Dichroic measurements for 1,2-ethanedithiol dibenzoate were made in the NaCl region on oriented crystal film obtained by differential cooling of a melt between rock-salt plates.

Results

Polyethylene Terephthalate.—Infrared spectra of polyethylene terephthalate and polyethylene-d_4 terephthalate in the range 10~32 μ are shown in Fig. 1. The frequencies of the bands observed below 750 cm^{-1} together with those reported by Tobin[6] are listed in Table I. Two bands at 575 and 422 cm^{-1} reported by Tobin were not observed though a band at 631 cm^{-1} which was reported as a weaker band than the above two was detected. None of the bands between 700~400 cm^{-1} showed perpendicular dichroism. Tentative assignments for some of the bands are given in the last column of Table I. The assignment of the $\mathrm{C\ddot{O}_2}$ rocking vibrations is supported by the fact that corresponding bands are found in ethylene glycol dibenzoate (480 cm^{-1}) and 1,2-ethanedithiol bis-(4-methoxycarbonylbenzoate) (488 cm^{-1}) but not in 1,2-ethanedithiol dibenzoate.

TABLE I. INFRARED FREQUENCIES (cm^{-1}) OF POLYETHYLENE TEREPHTHALATE

P. E. T.		P. E.-d_4. T.	Mode
Tobin	This work		
727(s) σ	727(s) σ	725(s) σ	
670(m)	680(w)		
628(w)[c]	631(w) π	631(w) π	aromatic vibration
575(m)			
508(s)[a] π	506(m)[c] π	502(m)[c] π	CO_2 rocking
500(s)[a]	500(m)[a]	530(m)[a]	
437(c) π	437(m)[c] π		C-C-O deformation
422(s)[a]			
382(s)[c]	379(s)[c]	364(s)[c]	C-O-C deformation

s: strong, m: medium, w: weak, a: amorphous band, c: crystalline band,
σ: perpendicular dichroism, π: parallel dichroism.

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[7] M. Margoshes and V. A. Fassel, *Spectrochim. Acta*, 7, 14 (1955).

[8] A. Miyake, *J. Polymer Sci.*, 38, 479 (1959).

* The author is indebted to Dr. Y. Mashiko et al. of the Government Chemical Industrial Research Institute, Tokyo, for the measurement in the CsBr region and to Dr. H. Tadokoro of Osaka University for the dichroic measurement for 1,2-ethanedithiol dibenzoate.

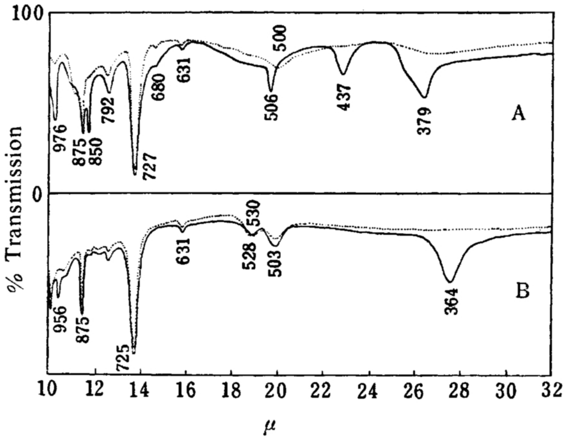

Fig. 1. Infrared spectra of polyethylene terephthalate (A) and polyethylene-d_4 terephthalate (B). …… quenched sample; —— annealed sample.

Thiol Esters. — Infrared spectra of the two thiol esters in the NaCl region are shown in Fig. 2 together with that of ethylene glycol bis-(4-methoxycarbonylbenzoate) previously reported[8]. It is apparent that the strong band at 727 cm^{-1} observed in ethylene glycol bis-(4-methoxycarbonylbenzoate) disappears in 1,2-ethanedithiol bis-(4-methoxycarbonylbenzoate), while the bands at 1502, 1408 and 1021 cm^{-1} in the former which are attributable to the vibrations of *p*-phenylene group by analogy with polyethylene terephthalate[3] also appear in the latter at substantially the same frequencies (1502, 1403, and 1016 cm^{-1}). Most of the strong bands observed in the latter can be attributed to the ester or thiol ester groups (Table II). The bands which arise from the thiol ester group are easily identified by their distinguished intensities in 1,2-ethanedithiol dibenzoate. The assignments for the vibrations of the thiol ester group given in Table II are consistent with the results of dichroic measurement which will be described next.

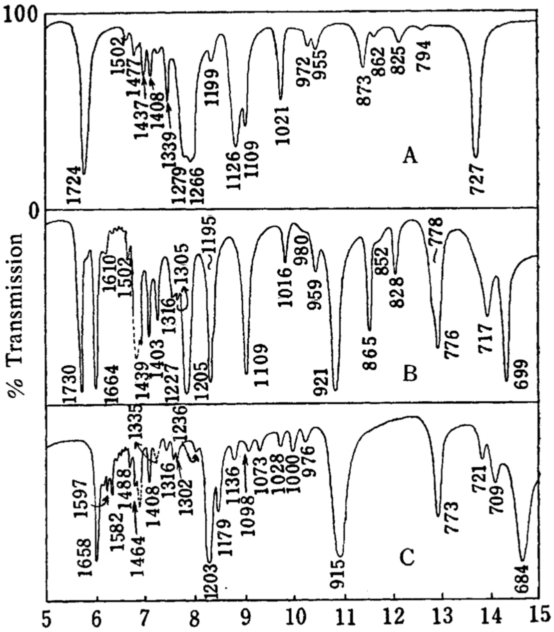

Fig. 2. Infrared spectra of ethylene glycol bis-(4-methoxycarbonylbenzoate) (A), 1,2-ethanedithiol bis-(4-methoxycarbonylbenzoate) (B) and 1,2-ethanedithiol dibenzoate (C).

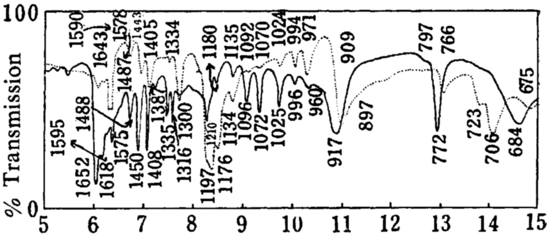

Fig. 3. Polarized infrared spectra of 1,2-ethanedithiol dibenzoate.

Dichroic Measurement for 1,2-Ethanedithiol Dibenzoate. — Fig. 3 shows the spectra of an oriented crystalline film of 1,2-ethanedithiol dibenzoate. The solid curve was run with the polarizer setting so that the electric vector of the polarized beam was perpendicular to the direction of the crystal growth of the sample.

TABLE II. VIBRATION OF ESTER AND THIOL ESTER GROUPS (cm^{-1})

$(CH_3O_2CC_6H_4CO_2CH_2\text{-})_2$	$(CH_3O_2CC_6H_4COSCH_2\text{-})_2$	$(C_6H_5COSCH_2\text{-})_2$	Assignment
1724	1730		C=O stretching
	1664	1658	C=O stretching
1279, 1266	1277		C-O-C asym. stretching
	1205	1203	C-S-C asym. stretching
972	1109		C-O-C sym. stretching
	921	915	C-S-C sym. stretching
	776	773	COS out-of-plane bending
	717		CO_2 in-plane bending
	699	684	COS in-plane bending

The dotted curve was run with the sample in the same position but with the polarizer rotated 90° from the first position. The C=O stretching (1652 cm^{-1}) and C–S–C antisymmetric stretching (1197 cm^{-1}) bands whose assignments are certain, show perpendicular and parallel dichroisms respectively. Further, a band at 1450 cm^{-1} attributable to CH_2 bending vibrations shows perpendicular dichroism and a band at 1300 cm^{-1} attributable to CH_2 wagging vibrations shows parallel dichroism. From these facts, it follows that the chain CO–S–CH_2–CH_2–S–CO is essentially parallel to the direction of crystal growth. On the other hand, bands attributable to in-plane vibrations of the phenyl group by analogy with toluene and monodeutero benzene show perpendicular dichroism, while bands attributable to out-of-plane vibrations show parallel dichroism (Table III). This indicates that the plane of the phenyl group is approximately normal to the direction of crystal growth. Based on these results, the probable configuration and arrangement of the molecule** are shown in Fig. 4. The dichroisms observed for the three strong bands at 917, 772 and 684 cm^{-1} which were assigned, respectively, to the C–S–C symmetric stretching, COS out-of-plane bending, and COS in-plane bending vibrations are in agreement with those expected from the above arrangement.

TABLE III. VIBRATION OF PHENYL GROUP (cm^{-1})

Mode[a)]		C_6H_5D[9)]	$C_6H_5CH_3$[10)]	$(C_6H_5COSCH_2\text{-})_2$
In-plane	8 b	1574	1586	1575(σ)
	19 a	1480	1483	1488(σ)
	19 b	1450	1310	1316(σ)
	15	1076	1070	1072(σ)
	18 a	1031	1030	1025(σ)
Out-of-plane	5	995	943	994(π)
	17 a	970	(985)	971(π)
	17 b	922	890	890(π)
	10 b	850	730	723(π)
	4	698	695	706(π)

a) We owe the numbering of vibrational modes to Wilson [E. B. Wilson, Jr., *Phys. Rev.*, **45**, 706 (1934)].

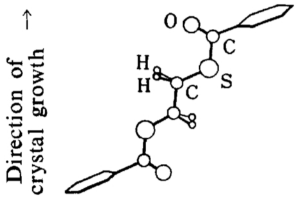

Fig. 4. Probable configuration of 1,2-ethane dithiol dibenzoate.

Discussion

Although a good deal of work has been done on the characteristic stretching frequencies of the ester group, no systematic study of the deformation frequencies has been carried out. Our knowledge of the factors influencing the frequency and intensity of the deformation vibrations is still relatively meager. Nevertheless, it is possible to predict the approximate position for some of them. Thompson and Torkington[11)] have found two characteristic bands of fair intensities at about 600 cm^{-1} for acetates and propionates (612 and 640 cm^{-1} for acetates and 590 and 610 cm^{-1} for propionates). Later, Wilmshurst[12)] has assigned the bands at 639 and 615 cm^{-1} in methyl acetate to CO_2 in-plane bending and CO_2 out-of-plane bending vibrations, respectively. In a number of α,β-unsaturated esters, Walton and Hughes[13)] have found strong bands at 850∼750 cm^{-1}, which have been reasonably assigned to the CO_2 out-of-plane vibration by their dichroic behaviors. A band of similar nature falls at 781 cm^{-1} in methyl oxalate[13)]. In the light of these results, the CO_2 out-of-plane bending vibration of aromatic esters is reasonably expected to appear above 600 cm^{-1}.

In either polyethylene terephthalate or polyethylene-d_4 terephthalate, however, no band attributable to the CO_2 out-of-plane bending vibration is observed in the range 700∼550 cm^{-1}. The bands at 680 and 631 cm^{-1} are too weak to be assigned to a CO_2 out-of-plane vibration, and moreover their dichroisms are inconsistent with that expected for an out-of-plane vibration. The polymer chain in a drawn sample of polyethylene terephthalate has been known to orient parallel to the direction of drawing[1,4,14)] and hence an out-of-plane vibration is expected to exhibit perpendicular dichroism. Since the absorption bands above 750 cm^{-1} in this polymer have been assigned with fair certainty[3)] to vibrations other than the CO_2 out-of-plane bending vibration, the only band left assignable to it is the strong and perpendicular band at 727 cm^{-1}.

There are three infrared-active out-of-plane

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9) C. K. Ingold et al., *J. Chem. Soc.*, **1946**, 299, 316.

10) K. S. Pitzer and D. W. Scott, *J. Am. Chem. Soc.*, **65**, 817 (1943).

** The crystal structure of this compound is not known. It is assumed that all the molecules take the same arrangement with respect to the direction of crystal growth. Configurations obtained from that shown in Fig. 4 by rotating the S-CO bond are also possible, but this does not affect the following discussions.

11) H. W. Thompson and P. Torkington, *J. Chem. Soc.*, **1945**, 640.

12) J. K. Wilmshurst, *J. Mol. Spectroscopy*, **1**, 201 (1957).

13) W. L. Walton and R. B. Hughes, *J. Am. Chem. Soc.*, **79**, 3985 (1957).

14) W. J. Dulmage and A. L. Geddes, *J. Polymer Sci.*, **31**, 499 (1958).

TABLE IV. INFRARED-ACTIVE OUT-OF-PLANE VIBRATIONS (cm^{-1})

Mode	C_6H_6[15]	p-$C_6H_4D_2$[16]	p-$C_6H_2D_4$[16]	C_6D_6[15]	p-$C_6H_4(CH_3)_2$[10]
16 b	405	367	383	350	389
11	673	597	548	496	(170)
17 b	975	876	925	793	796

vibrations for p-disubstituted benzenes (point group V_h). Some authentic frequencies for these vibrations are listed in Table IV together with those of benzene. Based on these frequencies, modes 16b and 11 in polyethylene terephthalate can be reasonably assumed to appear below 500 cm^{-1}. Hence, the only aromatic out-of-plane vibration expected to appear above 700 cm^{-1} is the mode 17b. It is unlikely that both the perpendicular bands (875 and 727 cm^{-1}) observed in polyethylene terephthalate can be assigned to aromatic out-of-plane vibrations.

It thus seems logical to consider that the band at 727 cm^{-1} is related to the CO_2 out-of-plane bending vibration. It should be noted that similar bands called the extra bands[7] are found in aromatic esters, acids, amides, and nitro compounds, all of which have out-of-plane bending vibrations of the substituents.

The band at 727 cm^{-1}, however, cannot be described as a pure CO_2 out-of-plane bending vibration, because it is removed by the deuteration of terephthalic acid residue[2,5]. This removal can be explained by assuming that the CO_2 out-of-plane bending mode and the 17b mode referred to above couple between each other. These two modes are similar in their frequencies and symmetry types. Therefore it is very probable that the perpendicular band at 875 and 727 cm^{-1} in polyethylene terephthalate arise from these coupled vibrations. The assumption of the coupling between the CO_2 and aromatic C–H out-of-plane bending vibration can also explain the anomalous shift of the latter in certain aromatic esters[7]. For example, the appearance of two bands at 809 and 711 cm^{-1} in methyl benzoate[8] may be explained as a consequence of this coupling, considering that pure frequencies for phenyl C–H and ester CO_2 out-of-plane bending vibrations fall at 770∼730 cm^{-1} and 800∼750 cm^{-1}, respectively. Furthermore, similar anomalies of C–H out-of-plane bending frequencies in some α,β-unsaturated esters seem also to result from an analogous coupling. The ethylenic C–H out-of-plane bending frequencies of acrylates and methacrylates fall outside the normal range, while those of crotonates lie close to the normal range (Table V). Based on the assumption that the ethylenic C–H and ester CO_2 out-of-plane bending vibrations in crotonates are substantially free of coupling and hence that the frequency of a pure out-of-plane vibration of an ester group attached to an ethylenic bond falls at about 840 cm^{-1}, the shifts in acrylates and methacrylates can be easily explained as the result of coupling between the ethylenic C–H and ester CO_2 out-of-plane bending vibrations. The frequency difference between the two pure modes is about 50 cm^{-1} in acrylates and methacrylates, while it amounts to about 120 cm^{-1} in crotonates.

TABLE V. C–H AND CO_2 OUT-OF-PLANE BENDING FREQUENCIES (cm^{-1}) FOR α,β-UNSATURATED ESTERS

Compound	π(C–H)	$\pi(CO_2)$	Normal position[17] for π(C–H)
Crotonates[13]	982∼970	842∼833	970∼960
Acrylates[13,18]	988∼981 967∼960	813∼808	995∼985 915∼905
Methacrylates[13,18]	943∼935	817∼813	895∼885

All these facts indicate the general occurrence of the coupling between CO_2 and C–H out-of-plane bending vibrations in aromatic esters. This coupling is, of course, destroyed when any one of the following conditions is not satisfied; first, similarity of frequencies of pure vibrations for the two modes, and second, coplanarity of the aromatic ring and the ester group.

1, 2-Ethanedithiol dibenzoate and 1, 2-ethanedithiol bis-(4-methoxycarbonylbenzoate) investigated in the present work provide further evidence for the interpretation developed above. As was shown in the section of experimental results, phenyl and thiol ester groups of the former compound are not present in the same plane, and hence no coupling is expected between the out-of-plane vibrations of the two groups. Therefore the perpendicular band at 773 cm^{-1} can be considered as an essentially pure COS out-of-plane bending vibration. Since the out-of-plane bending frequency of an ester group is expected not to be very different from that of a thiol ester group, the appearance of the latter at 773 cm^{-1} supports

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[15] F. A. Miller, *J. Chem. Phys.*, **24**, 996 (1956).

[16] S. C. Carson, R. R. Gordon and C. K. Ingold, *J. Chem. Soc.*, **1946**, 288.

[17] L. J. Bellamy, "The Infrared Spectra of Complex Molecules", 2nd Ed., Methuen, London (1958), p. 34.

[18] W. H. T. Davison and G. R. Bates, *J. Chem. Soc.*, **1953**, 2607.

the assumption adopted in the foregoing discussion that a pure out-of-plane bending vibration of an aromatic ester group falls at about 800 cm^{-1}. The aromatic out-of-plane vibration of this compound (721 and 709 cm^{-1}) falls close to the normal positions for phenyl groups (see Table III). In ethylene glycol dibenzoate[8], however, three bands were observed at 804, 695 and 683 cm^{-1}, but no band was observed in the normal range (770~720 cm^{-1}) for the mode 10b. This difference between the thiol ester and the ester can be again explained by the coupling between the out-of-plane vibrations. If one assumes that the CO_2 vibration couples with phenyl vibration, the lowering of the phenyl out-of-plane frequency in ethylene glycol dibenzoate is readily explained.

Two bands at 873 and 727 cm^{-1} in ethylene glycol bis-(4-methoxycarbonylbenzoate) undoubtedly correspond to the two perpendicular bands at 875 and 727 cm^{-1} in polyethylene terephthalate. The latter disappears and the former shifts to 865 cm^{-1} on going from ethylene glycol bis-(4-methoxycarbonylbenzoate) to 1, 2-ethanedithiol bis-(4-methoxycarbonylbenzoate). This change seems also to be accounted for by assuming that the aromatic ring and thiol ester group in the latter are not coplanar. The C–H out-of-plane vibration of the *p*-phenylene group and the CO_2 out-of-plane vibrations of the two ester groups in the former compound couple amoung each other giving rise to two bands at 873 and 727 cm^{-1}. On the other hand, in the latter compound, at least the vibration of the thiol ester group may not be coupled with the aromatic vibration, and hence their frequencies are different from those of the former compound. It is not known whether the ester and *p*-phenylene groups in 1, 2-ethanedithiol bis-(4-methoxycarbonylbenzoate) are coplanar or not, but in any case the bands at 865 and 778 cm^{-1} (shoulder) are attributable to the out-of-plane vibrations of these two groups. It is difficult to explain the spectral difference between the two model compounds on the basis of assigning both the bands at 873 and 727 cm^{-1} cited above to aromatic out-of-plane vibrations.

In conclusion, the bands at 875 and 727 cm^{-1} in polyethylene terephthalate can be reasonably assigned to coupled vibrations of aromatic C–H and ester CO_2 out-of-plane bending modes which provide a consistent explanation for several aromatic esters and thiol esters.

Finally, mention should be made of the CO_2 in-plane bending frequency. Since this is expected not to be very different from that of the COS in-plane bending vibration, that band at 717 cm^{-1} in 1, 2-ethanedithiol bis-(4-methoxycarbonylbenzoate) can probably be assigned to this mode. It is possible that this vibration in polyethylene terephthalate lies buried under the band at 727 cm^{-1}.

Summary

Infrared spectra of polyethylene terephthalate and polyethylene-d_4 terephthalate were investigated in the KBr and CsBr regions. No band attributable to a CO_2 out-of-plane bending vibration was found below 700 cm^{-1}. The only band assignable to this mode is a strong and perpendicular band at 727 cm^{-1}. This fact together with the disappearance of the 727 cm^{-1} band in polyethylene deuteroterephthalate, indicates that two bands at 875 and 727 cm^{-1} in polyethylene terephthalate can be assigned to coupled vibrations of aromatic C–H and ester CO_2 out-of-plane bending modes. This interpretation provides a consistent explanation for the spectral differences between ethylene glycol dibenzoate and 1, 2-ethanedithiol dibenzoate and between ethylene glycol bis-(4-methoxycarbonylbenzoate) and 1, 2-ethanedithiol bis-(4-methoxycarbonylbenzoate) as well as for the anomalous shifts of C–H out-of-plane frequencies and the appearances of "extra bands" in several aromatic esters.

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Note Added in Proof:

Recently, perpendicular bands at about 820 cm^{-1} have been found in polyethylene terephthalate-d_4 and polyethylene d_4 terephthalate-d_4 [C. Y. Liang and S. Krimm, *J. Mol. Spectroscopy*, **3**, 554 (1959).]. These bands can be assigned to the CO_2 out-of-plane vibration in these deuteroterephthalates. If this assingnment is correct, it seems better to consider that the 17b vibration of the terephthalates has a lower frequency than the CO_2 out-of-plane vibration. Then, for the band at 727 cm^{-1} in polyethylene terephthalate, the contribution of the 17b vibration may exceed that of the CO_2 vibration, and vice versa for the band at 875 cm^{-1}[1].