Intensities of Vibration Bands. Part VI. Alkyl Esters.*

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The intensities of the vibrational absorption bands of some esters near 1200 cm.$^{-1}$ have been determined, extending previous results of Francis. Most of the compounds give approximately the same value for this intensity, although methyl esters show a small but significant difference. The composite nature of the band has been discussed and possible explanations have been suggested. The effect of different solvents upon the band intensity has been determined, and the values have been compared with that found in the gas phase. The results suggest that the Onsager relation for the intensity in the two phases is satisfactory.

THE use of molecular vibration frequencies in structural diagnosis is well established. Interest is now moving towards the use of vibrational band intensities to provide further structural information, but the best way of doing this cannot be assessed until more is known about the strength of key absorption bands in different molecules or of a given band in different physical environments. The intensities of several absorption bands of esters and ketones were recently determined by Francis (*J. Chem. Phys.*, 1951, **19**, 942). While his main interest lay in the band due to CH_3 and CH_2 groups, Francis also gave values for the bands near 1720 and 1200 cm.$^{-1}$ in a few molecules. The former band is characteristic of the stretching vibration of the carbonyl groups. That near 1200 cm.$^{-1}$ was found by Thompson and Torkington (*J.*, 1945, 640) to be intense with many esters and was assigned to a mode largely controlled by stretching of the C–O bond, although Francis has given arguments suggesting that it also involves some participation of the contiguous carbonyl group. Some years ago the intensity of this band near 1200 cm.$^{-1}$ in a series of esters was measured in this laboratory by Orr (Diss., Oxford, 1949), and we have recently repeated and extended his measurements. Since our results cover a wider range of compounds than was studied by Francis and reveal details not mentioned by him, an account is given below.

The band near 1200 cm.$^{-1}$ is not always single, but with many esters has at least two and probably more components. In formates, a close pair of bands lies between 1150 and 1220 cm.$^{-1}$, the components moving closer together as the alkyl chain lengthens. The band at lower frequency is usually the weaker, and its relative intensity falls in passing up the series. With acetates, there appears at first sight to be a single band, but closer inspection

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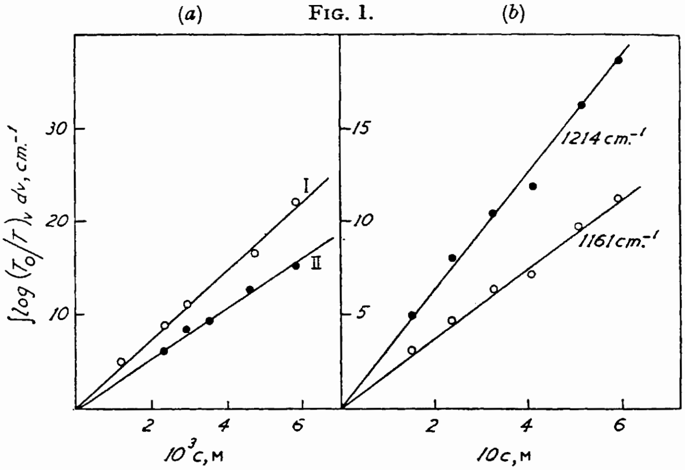
* Parts I—V; *Proc. Roy. Soc.*, 1948, *A*, **192**, 498; *Trans. Faraday Soc.*, 1950, **46**, 103; *Proc. Roy. Soc.*, 1951, *A*, **208**, 332, 341; *ibid.*, 1954, *A*, in the press.

suggests another doublet, the higher-frequency component being very weak in methyl acetate but increasing in relative intensity along the series. In methyl propionate the split is clear, as also indicated by Francis, but with higher propionates the components are inseparable. Reference to the previous spectral charts shows that the separate components are clearly seen with butyrates and *iso*butyrates, and where higher alkyl radicals are present more than two bands may occur. The exact location of the bands is different for the different sets of homologues, and is only affected slightly by the solvent used.

For the band areas, $B' = \int \ln (T_0/T)_\nu \,.\, d\nu$, where T_0 and T denote the apparent transmitted energy as opposed to the true values I_0 and I and this was determined by graphical integration of the plots of $\ln (T_0/T)_\nu$ against ν. B' was determined for a series of concentrations (c) and the linearity of the plots of B' against c showed that extrapolation by the method of Wilson and Wells (*J. Chem. Phys.*, 1946, **14**, 578) was not necessary. The slope of the plots gave B_0 and the true band intensity $A = (1/cl.)\int \ln (I_0/I)_\nu \,.\, d\nu$ was then given by B_0/l. The units used were: concentration in molecules per c.c., path length in cm., frequency in cycles per sec., with natural logarithms.

FIG. 1.



(*a*) Path length, 0·237 cm. I, *n*-Propyl acetate; II, ethyl propionate.

(*b*) Path length, 0·004 cm. Methyl formate.

We have measured the values of A for the "total" band near 1200 cm.$^{-1}$. Fig. 1(*a*) shows typical plots for *n*-propyl acetate and ethyl propionate, and the results are summarised in Table 1. Although no special procedure was used to apply wing corrections to the band areas (Ramsay, *J. Amer. Chem. Soc.*, 1952, **74**, 72), the values given are probably reliable to ±5%. Table 1 also includes Francis's results, and those of Orr,

TABLE 1. *Values of* 10^8A *in units cm.*^{2} *molecule*$^{-1}$ *sec.*$^{-1}$.

Substance	Francis (CCl_4)	Orr (MeCN)	Present work (CS_2)	Substance	Francis (CCl_4)	Orr (MeCN)	Present work (CS_2)
Methyl formate ...	—	147	130	*iso*Butyl acetate	—	—	176
Ethyl formate	—	170	169	*sec.*-Butyl acetate	—	—	187
n-Propyl formate ...	—	164	152	*n*-Amyl acetate ...	—	163	176
n-Butyl formate ...	—	176	165	Methyl propionate	129	116	126
*iso*Butyl formate ...	—	—	168	Ethyl propionate...	150	140	134
Methyl acetate	139	144	125	*n*-Butyl propionate	—	144	—
Ethyl acetate	176	166	165	*iso*Butyl propionate	—	—	149
n-Propyl acetate ...	177	164	180	*n*-Amyl propionate	—	140	—
*iso*Propyl acetate ...	—	—	170	Dimethyl carbonate	—	—	318
n-Butyl acetate ...	—	—	170	Diethyl carbonate	—	—	350

although the latter may be somewhat less accurate. The data show that for all the simple aliphatic monobasic acid esters about the same value is found for the intensity. However, the value for the methyl ester of an acid is significantly lower than for the higher homologues. It is possible that with the propionates the intensity is lower than with acetates and formates by an amount which exceeds plausible experimental error. It should be noted that the values for the two alkyl carbonates are about twice that for an ester containing a single ester group. This might imply that the method could be used for determining the number of alkoxycarbonyl groups in a molecule, but this is not very likely, since apart from other considerations it may be difficult in more complex cases to identify the bands concerned. It is interesting that the resonance energy of carbonates (40—50 kcal./mole) is roughly double that of the simple alkyl esters (17—25 kcal./mole) (Pauling, " The Nature of the Chemical Bond," Cornell Univ. Press, 1939 ; Wheland, " Theory of Resonance," Wiley, New York, 1944), supporting the correlation of this property with the band intensity (Barrow, *J. Chem. Phys.*, 1953, **21**, 2008).

Now, with the formates it is possible to estimate the individual contributions of each of the " pair " of bands ν_a, ν_b near 1200 cm.$^{-1}$. Table 2 summarises the results found by Orr, the results for methyl formate being shown in more detail in Fig. 1(*b*). With the acetates, the separation of the severely overlapping bands made the estimation of separate band areas (in parentheses in Table 2) somewhat artificial, although the trends are undoubtedly as indicated by the results. It would, of course, have been possible to select one or other of the " pair " of bands as due to the vibration concerned, and to infer that in formates the intensity varies steadily along a homologous series. The regularity of the values of the total band area suggests, however, that it is more reasonable to include the " total " band areas in all cases. Francis appears to do this in the case of methyl propionate.

TABLE 2.

Solvent : acetonitrile

Values of A in cm.^{2} molecule^{-1} sec.$^{-1}$.

Substance	ν_a	10^8A	ν_b	10^8A	Total 10^8A
Methyl formate	1161	54·3	1214	92·5	147
Ethyl formate	1155	30·5	1195	140	170
n-Propyl formate	1154	25·6	1190	138·3	164
n-Butyl formate	1151	14·4	1186	162	176
Methyl propionate	1178	19·9	1208	96·1	116
Methyl acetate	1253	133	1288	10·6	144
Ethyl acetate	1249	(147)	1273	(19)	166
n-Propyl acetate	1246	(106)	1268	(58)	164
n-Amyl acetate	1246	(76·5)	1260	(86)	163

We must, then, interpret the doubling of the band, or indeed the possibility that it may have several components. Thompson and Torkington (*J.*, 1945, 640) suggested that the C–O–R part of the alkoxycarbonyl group might have two vibrations connected with the C–O–C part of the skeleton. The somewhat anomalous result with methyl esters might support this hypothesis, as might also the rough equality of ν_a and ν_b with methyl formate.

An alternative interpretation would be to assume the occurrence of rotational isomers. Similar observations have been described by Jones, Humphries, Herling, and Dobriner (*J. Amer. Chem. Soc.*, 1951, **73**, 3215) for the 3-acetoxy-steroids, and they have explained them in this way. The investigation of rotational isomerism in esters by measurements of dipole moment has given only inconclusive evidence.

The effect of the solvent upon the relative intensities of the components of a " pair " should be mentioned. With methyl formate in acetonitrile the ratio of the molar extinction coefficients of ν_b and ν_a is about 1·2, whereas in carbon disulphide it is about 0·9. This effect might arise, however, from the effect of differences in bonding power of the solvents upon one component of the band pair if it involves participation of the carbonyl group.

Some measurements were carried out with methyl formate to compare its total band intensity at 1200 cm.$^{-1}$ in the gas phase and in various solvents. For the vapour a cell 10·3 cm. in length was used, and Fig. 2 shows the plot of B' against the partial pressure of vapour, dry air being added up to 1 atm. Table 3 gives the values for A_g and A_s. The effect of a dielectric medium of refractive index n upon the absorption by a dipole has been

TABLE 3. *Values of* A *in cm.*^{2} *molecule*$^{-1}$ *sec.*$^{-1}$ ($\log_e$).

Solvent	n_D	10^8A	A_s/A_g
Vapour	—	149	1·00
Acetonitrile	1·342	159	1·06
Methylene chloride	1·420	152	1·02
Ethylene dichloride	1·442	149	1·00
Carbon tetrachloride	1·457	148	0·99
Benzene	1·497	146	0·98
Tetrachloroethylene	1·502	145	0·97
Carbon disulphide	1·624	130	0·87
Methylene iodide	1·738	117	0·79

considered by Debye (*Handb. Radiologie*, 1933, **6**, 69) and by Onsager (*J. Amer. Chem. Soc.*, 1936, **58**, 1486). They have suggested values for γ in the relation, $A_s = A_g\gamma^2/n$; γ is the ratio of the internal electric field on the solute molecule to the external field, and is given by one or other of the following expressions :

$$\gamma = (n^2 + 2)/3 \text{ (Debye)}; \; \gamma = 3n^2/(2n^2 + 1) \text{ (Onsager)}$$

Fig. 3 shows how the ratio A_s/A_g would be expected to vary with the refractive index for each of the theories, and also the ratio actually measured in the present work. Although the measured values of A_s/A_g cannot be regarded as very precise owing to plausible errors of say 5% in the measured band areas, they indicate a surprisingly good agreement with Onsager's expression over a wide range. In any case the results show that alteration of solvent does not markedly affect the intensity of the band studied unless the refractive index is high. This result may be of general interest since few measurements of this kind seem yet to have been made.

FIG. 2.

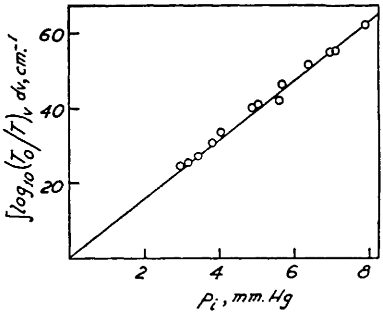
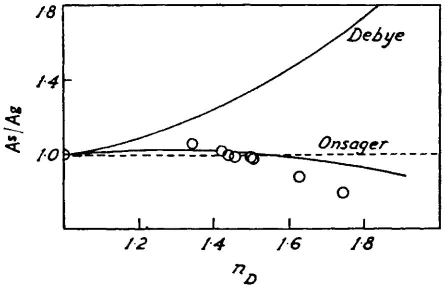


FIG. 3.



Experimental.—The spectrometers used were a Perkin-Elmer 12C instrument, and a similar rock-salt prism spectrometer built in this laboratory. In both cases the effective slit widths were 3—4 cm.$^{-1}$, which is much less than the widths of the absorption bands. Scattered radiation errors were eliminated by means of a quartz shutter. Absorption cells were made in the usual way with rock-salt plates, and their thickness was determined from measured absorption bands of solutions by reference to a much thicker cell whose dimensions could be accurately measured. Solvents were purified according to Weissberger and Proskauer ("Organic Solvents," Oxford Univ. Press, 1935). The esters were repurified by fractionation and stored over anhydrous calcium sulphate.

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