281. *The C–H Stretching Bands of Methoxyl Groups.*

By H. B. Henbest, G. D. Meakins, B. Nicholls, and A. A. Wagland.

Methoxyl groups in organic compounds can be detected by a characteristic band in the 2832—2815 cm.$^{-1}$ region of the infrared spectrum.

The pioneering work of Fox and Martin[1] on the CH stretching frequencies of methyl, methylene, and methine groups has been extended in recent years by some careful studies of the 3000 cm.$^{-1}$ region of hydrocarbons.[2] Within a restricted field—for example, saturated aliphatic hydrocarbons[2b]—spectra can be analysed fairly exactly in terms of the CH stretching vibrations of non-interacting $-CH_3$, $>CH_2$, and $\geqslant CH$ units. But with most organic compounds this simple idea cannot be applied:[3] the complex spectra are difficult to interpret and so far their main use has been in detecting olefinic bonds by the presence of peaks or shoulders on the high-frequency side of the main CH stretching bands.

In an attempt to obtain more information from this region of the spectrum a series of methyl ethers shown in the Table have been studied over the 3100—2800 cm.$^{-1}$ range.

Comparison of the methyl ethers and reference compounds (Table) provides clear evidence that the methoxyl group is associated with a characteristic band G (2832—2819 cm.$^{-1}$) appearing on the low-frequency side of the main CH absorption. The appearance of the spectra of three compounds containing no methyl, a *C*-methyl, and an *O*-methyl group respectively, is illustrated in the Figure. It is important that band G is not given by *C*-methyl groups (cf. nos. 1 and 2, 4 and 5) or by ethoxyl groups (cf. nos. 12 and 13, 14 and 15, 21 and 22). For compounds nos. 2, 3, 6—9, 13, 15, and 16, which are of roughly comparable molecular weight and have each one methoxyl group, the intensity of band G is between 35 and 75 units; with two methoxyl groups (nos. 10 and 11) the intensity is about 120 units. It is noteworthy that the band still appears in methoxy-steroids (nos. 18—20) where the ratio of OMe to CH_2 and *C*-Me groups is much lower than in the acyclic and monocyclic examples. (Compare the behaviour of steroid *vic.*-epoxides[4] where the characteristic epoxide band is swamped by the main CH absorptions.) The correlation should be useful in supplementing the detection of methoxyl groups by a band near 1100 cm.$^{-1}$ recently studied in methoxy-steroids by Page.[5]

The simplest analysis of paraffinic CH stretching bands involves consideration of four main vibrations, *viz.*, antisymmetric and symmetric CH stretching of methyl and methylene groups. (The CH band of the methine group at about 2890 cm.$^{-1}$ is variable in frequency and weaker than the others.) In aliphatic systems the bands are near 2960, 2870 cm.$^{-1}$ (CH_3) and 2925, 2850 cm.$^{-1}$ (CH_2).[2b] While four (and only four) peaks are

---

[1] Fox and Martin, *Proc. Roy. Soc.*, 1938, *A*, **167**, 257; 1940, *A*, **175**, 208.

[2] (*a*) Plyler and Acquista, *J. Res. Nat. Bur. Stand.*, 1949, **43**, 37; Francis, (*b*) *J. Chem. Phys.*, 1950, **18**, 861; (*c*) *Analyt. Chem.*, 1952, **24**, 604; 1953, **25**, 1466.

[3] Pozefsky and Coggeshall, *ibid.*, 1951, **23**, 1611.

[4] Henbest, Meakins, Nicholls, and Taylor, preceding paper.

[5] Page, *J.*, 1955, 2017.

CH *stretching bands (cm.$^{-1}$) of methyl ethers and, in square brackets, reference compounds.*

The compounds were examined in CCl_4 solution on a Perkin-Elmer Model 21 double-beam spectrometer fitted with a calcium fluoride prism. Figures in parentheses are molecular extinction coefficients (mole^{-1} l. cm.$^{-1}$) units. No intensity values are given for shoulders (sh) on the sides of main bands. Various compounds (in square brackets) not containing methoxy-groups are included in the Table for reference. The bands are divided into frequency ranges, and each column is designated by a letter as shown.

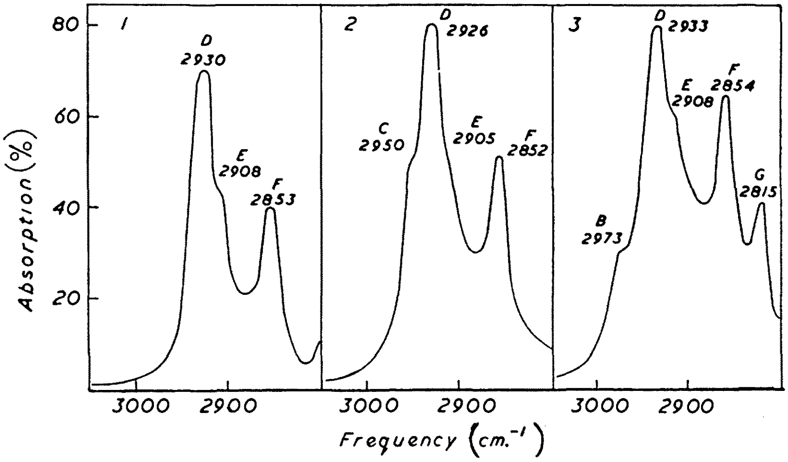
No.		A	B	C	D	E	F	G
		3100–3000	3000–2970	2970–2950	2950–2920	2920–2890, 2880	2890, 2880–2840	2840–2810
	Acyclic compounds							
[1	Di-*n*-butyl ether]			2960(250)	2933(220)		2865(205)	
2	*n*-Hexyl methyl ether		2990 sh	2958(140)	2929(170)		2863(125)	2825(55)
3	*trans*-Hex-3-en-1-yl methyl ether	3030(20)	2985 sh	2868(110)	2928(110)	2894(90)	2872(95)	2823(60)
	cyclo*Hexane derivatives*							
[4	*cyclo*Hexane]				2930(>275)	2908 sh	2853(180)	
[5	Methyl*cyclo*hexane]			2950 sh	2926(>285)	2905 sh	2852(215)	
6	Methoxy*cyclo*hexane		2973 sh		2933(280)	2908 sh	2854(155)	2815(75)
7	*trans*-4-Methoxy*cyclo*hexanol		2978 sh		2938(200)	2908 sh	2862(110)	2820(45)
8	*cis*-4-Methoxy*cyclo*hexanol		2978 sh		2943(210)		2864(100)	2822(45)
9	4-Methoxy*cyclo*hexanone		2978 sh		2941(120)	2893 sh	2876(70)	2824(45)
10	*trans*-1 : 4-Dimethoxy*cyclo*hexane		2982(80)		2943(240)	2905 sh	2864(135)	2821(115)
11	*cis*-1 : 4-Dimethoxy*cyclo*hexane		2980(55)		2943(240)	2905 sh	2864(120)	2819(120)
	cyclo*Hexene derivatives*							
[12	3-Ethoxy*cyclo*hexene]	3034(30)	2982(75)		2944(103)		2870(75) 2846 sh	
13	3-Methoxy*cyclo*hexene	3034(25)	2983 sh		2943(95)		2878 sh 2840 sh	2818(40)
[14	4-Ethoxy*cyclo*hexene]	3028(25)	2975(75)		2928(95)		2878 sh 2844(65)	
15	4-Methoxy*cyclo*hexene	N.I.	2975(50)		2923(185)	2898 sh	2863 sh 2840(75)	2820(65)
16	*endo*-4-Methoxy*bicyclo*[2 : 2 : 1]hept-1-ene	3068(25)	2981(145)		2938(105)	2895 sh	2862(55)	2819(35)
	Steroids							
[17	Cholest-5-en-3β-ol]	3028 sh		2958 sh	2938(>385)		2868(275) 2857 sh	
18	3β-Methoxycholest-5-ene	3033 sh		2953 sh	2938(395)		2868(220) 2853 sh	2828(115)
19	3β-Methoxyergosta-7 : 22-dien-11-one			2958(345)	2933(285)		2868(220)	2820(75)
20	3β-Methoxyergosta-8 : 22-dien-11-one			2958(410)	2938 sh		2869(265)	2823(90)
	Aromatic compounds							
[21	Phenetole]	3068(15) 3038(20) 2983(60)			2928(30)	2903(30)	2875(30)	
22	Anisole	3068(20) 3033(25) 3000(30)			2948(45)	2908(30)		2832(40)
23	Veratrole	N.I.			2948(60)	2904(40) 2892 sh		2832(60)

N.I. = not investigated in this region.

Materials. Nos. 3, 7, 8, 10, 11, 14, 15, and 16: Henbest and Nicholls, unpublished work. 19 and 20, Jones, Meakins, and Stephenson, unpublished work. The remaining compounds were prepared by published methods, or by purification ot commercial products.

found in a few series, such as the esters of the long-chain acids,[6] the spectra of most compounds are rendered complex by the occurrence of vibrational coupling, etc. (for an example see the discussion by Plyler and Acquista [2a] of the CH stretching region of *cyclo*hexane and *cyclo*pentane hydrocarbons).

In view of these factors it is impracticable to make rigid assignments of bands A—G. However, it seems possible to associate them for the first 20 compounds with structural features as follows : (A) CH stretching of olefinic groups.[7, 8] Antisymmetric CH stretching of (B) CH_3 in OEt and OMe groups ; (C) CH_3 in *C*-Me groups ; and (D) CH_2 in all types of methylene group. (E) Where present, probably due to CH_2 groups. (F) Symmetric CH stretching of CH_2 in all types of methylene group and CH_3 in *C*-Me and OEt groups.



1, cyclo*Hexane*. 2, *Methyl*cyclo*hexane*. 3, *Methoxy*cyclo*hexane*.

(G) Symmetric CH stretching of CH_3 in OMe groups. This was developed by considering the bands of compounds nos. 4, 5, and 6, and applying the deductions from these to the other examples. Clearly the observed peaks and shoulders are merely the sum totals of many partially overlapping bands : it must be stressed therefore that the specified vibrations are to be regarded as the ***main*** modes, but by no means the only ones, leading to the various bands. The most important correlation, relating band G to the methoxyl group, implies that connection of methyl to oxygen instead of carbon lowers the frequency of the symmetric CH_3 stretching mode by about 50 cm.$^{-1}$. Band B (thought to be associated with methyl in methoxyl and ethoxyl groups) shows a shift in the opposite direction for the antisymmetric methyl vibration : this correlation has been noted previously for ethoxyl groups.[3]

In the aromatic compounds (nos. 21—23) the bands above 3000 cm.$^{-1}$ are due to aromatic CH stretching, and those at 2832 cm.$^{-1}$ (nos. 22 and 23) are again associated with methoxyl, but more examples are needed for detailed analysis of the spectra.

We are grateful to the Department of Scientific and Industrial Research for a grant (to B. N.) and to Miss W. Peadon for technical assistance.

THE UNIVERSITY, MANCHESTER, 13.
[*Received, October* 12*th*, 1956.]

---

[6] Sinclair, McKay, Myers, and Jones, *J. Amer. Chem. Soc.*, 1952, **74**, 2578.
[7] Bladon, Fabian, Henbest, Koch, and Wood, *J.*, 1951, 2402.
[8] Henbest, Meakins, Nicholls, and Wilson, *J.*, 1957, 997.