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Analytical Applications of Raman Spectroscopy in Organic Chemistry: Influence of the Position, Stereochemistry and Substitution Pattern of the Double Bond on the ν(C=C) and ν(sp^2-CH) Stretching Bands in the Raman Spectra of Alkenyl Methyl Ethers

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The Raman spectra of 29 alkenyl methyl ethers, $C_nH_{2n-1}OMe$, of diverse structure containing up to seven carbon atoms reveal reliable correlations between the wavenumber of the ν(C=C) and ν(sp^2-CH) stretching bands and the position, stereochemistry and substitution pattern of the double bond.

Raman spectroscopy[1] has been applied less extensively than IR spectroscopy in organic chemistry. However, recent advances, particularly the advent of modern laser-Fourier-Transform instruments,[2,3] which permit Raman spectroscopy on a milligram or less of material in a few minutes, have opened the way for the application of Raman spectroscopy as a non-invasive technique for *in vivo* studies of skin, nail and other tissue samples.[4] Furthermore, the vibrational stretching modes associated with certain functional groups which are inactive or weak in the IR give rise to intense Raman bands. One such functional group is the C=C entity, which is of great biological significance, as shown by the importance of retinols, carotenoids and related compounds; thus, a comprehensive Raman spectroscopic study of carotenoids has been made.[5]

Unfortunately, however, the application of Raman spectroscopy in such systems is hindered by the imprecise correlation between the structure of the substrate and the associated bands. Thus, a Raman study[6] of a simple model compound, allyl methyl ether, and four ^{2}H- and ^{13}C-labelled analogues revealed that several tentative assignments of bands in the spectra of materials containing sp^2 and sp^3 C—H, C—C and C=C bonds were incorrect.

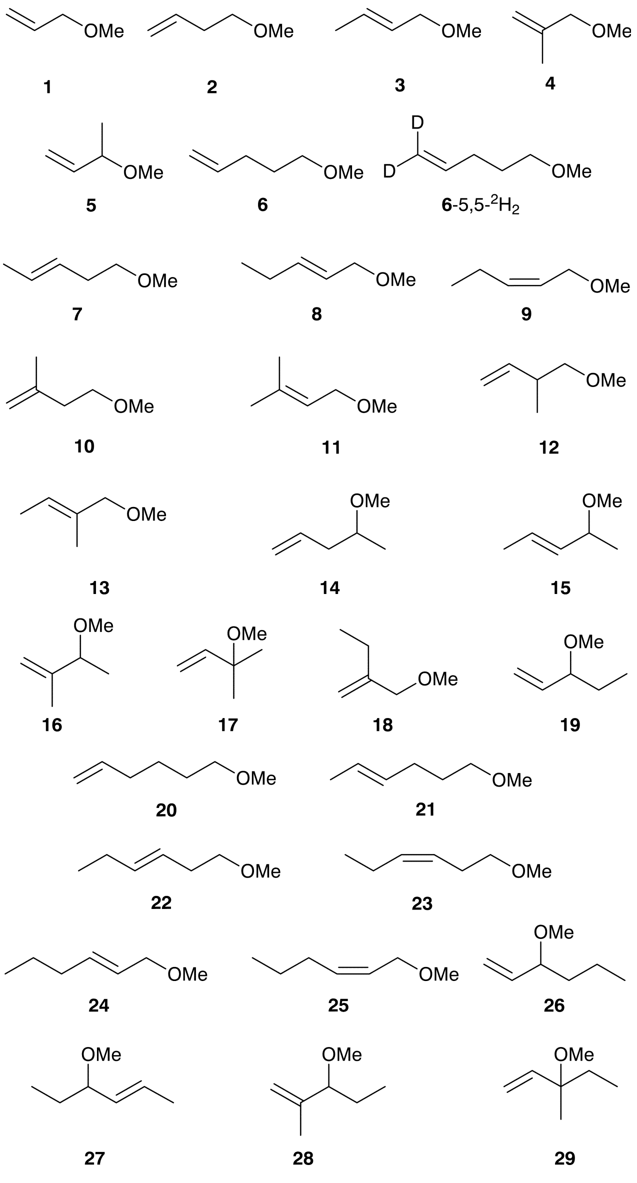
The structures of the 29 alkenyl methyl ethers investigated are shown in the Scheme. Relevant data on the important bands in the Raman spectra corresponding to C=C and C—H stretching vibrations are summarized in Table 1.

All these ethers showed a strong Raman band in the region 1640–1680 cm^{-1} associated with the stretching vibration of the C=C bond. In contrast, the corresponding absorptions in the IR spectra of at least some of these ethers were found to be extremely weak or not observable. Significant Raman bands were usually found for the related sp^2 C—H vibrations, though these bands were sometimes obscured by stronger bands associated with vibrations of the sp^3 C—H bonds.

The following correlations between the structural features of the ethers and their Raman spectra are evident.

First, the band associated with the C=C stretching vibration of a monosubstituted double bond appears between 1640 and 1645 cm^{-1}. An exception is **1**, for which the band is at slightly higher wavenumber (1648 cm^{-1}).

Secondly, the wavenumber of the band in 1,2-disubstituted systems depends systematically on the stereochemistry of the double bond: *trans*-geometrical isomers show a band at higher wavenumber (typically 1670–1675 cm^{-1}) than their *cis*-isomers (normally 1655–1660 cm^{-1}).



Scheme

Thirdly, the band in the spectra of ethers containing a 1,1-disubstituted C=C entity appears in roughly the same

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Table 1 C=C and sp^2 C—H stretching bands in the Raman spectra of alkenyl methyl ethers

Compound	Nature of C=C entity[a]	ν(C=C)[b,c]	ν(sp^2-C—H)[b,c]
1	1-monosubstituted	1648	3084, 3017, 2985
2	1-monosubstituted	1642	3082, 3003, 2982
3	*trans*-1,2-disubstituted	1675	3009, 2983
4	1,1-disubstituted	1658	3079, 2986
5	1-monosubstituted	1644	3083, 3007, 2984
6	1-monosubstituted	1641	3080, 2998, 2982w
6-5,5-$^2H_2$	1-monosubstituted	1602	2999, 2308, 2215
7	*trans*-1,2-disubstituted	1673	3004, 2982w
8	*trans*-1,2-disubstituted	1672	3004
9	*cis*-1,2-disubstituted	1658	3017
10	1,1-disubstituted	1650	3077, 2984
11	1,2,2-trisubstituted	1678	3026w, 3016w
12	1-monosubstituted	1641	3082, 2996, 2983
13	1,1,2-trisubstituted	1676	2974?
14	1-monosubstituted	1642	3080, 2999, 2979
15	*trans*-1,2-disubstituted	1675	2998
16	1,1-disubstituted	1653	3075, 2985
17	1-monosubstituted	1645	3087, 3008, 2982
18	1,1-disubstituted	1653	3077, 2985
19	1-monosubstituted	1644	3081, 3005, 2982
20	1-monosubstituted	1642	3080, 2998
21	*trans*-1,2-disubstituted	1672	3000w, 2882
22	*trans*-1,2-disubstituted	1670	3000w
23	*cis*-1,2-disubstituted	1656	3011
24	*trans*-1,2-disubstituted	1672	3003w
25	*cis*-1,2-disubstituted	1658	3018
26	1-monosubstituted	1643	3081, 3005, 2982
27	*trans*-1,2-disubstituted	1672	2999
28	1,1-disubstituted	1650	3074, 2984
29	1-monosubstituted	1641	3086, 3006, 2981

[a] For the purposes of defining the substitution pattern of the double bond, carbon 1 is regarded as being that nearer to the methoxy group. [b] All values quoted in cm^{-1} and rounded to the nearest integer; 'w' denotes a weak or ill-defined band. [c] The FT-Raman spectra were recorded using a Bruker FRA 106 Raman module on a Bruker IFS66 optics system. The spectra were corrected for instrument response; the observed band wavenumbers, which were calibrated against the internal laser frequency, are correct to better than ±1 cm^{-1}.

wavenumber range (1650–1660 cm^{-1}) as is found for *cis*-1,2-disubstituted species.

Fourthly, in systems containing a trisubstituted double bond, the band appears at only marginally higher wavenumber than those of *trans*-1,2-disubstituted species.

Further complementary trends are evident in the wavenumber of the associated sp^2 C—H stretching vibration(s) for monosubstituted and 1,2-disubstituted ethers. Both classes of ether show a band in each of the ranges 3087–3075 and 2986–2979 cm^{-1}; these bands may be attributed to the asymmetric‡ and symmetric C—H stretching vibrations, respectively, of the terminal $C{=}CH_2$ group. Monosubstituted ethers show an additional band in an intermediate range (usually 3008–2998 cm^{-1}).

The band at intermediate wavenumber has often been ascribed to the asymmetric (or 'antisymmetric') C—H stretching vibration of the terminal methylene group of the $CH{=}CH_2$ entity; but such an interpretation is incorrect because this band is not present in the spectra of 1,1-disubstituted ethers, which instead show a band in each of the ranges 3087–3075 and 2986–2979 cm^{-1}. Moreover, the spectra of other ethers containing a non-terminal sp^2 C—H bond generally show a band in the intermediate wavenumber range.

The revised assignment of these bands is confirmed by the Raman spectrum of $CD_2{=}CHCH_2CH_2CH_2OCH_3$, **6**-5,5-$^2H_2$, which contains important bands at 2999, 2308 and 2215 cm^{-1}. The band at 2999 cm^{-1} is at practically the same wavenumber (2998 cm^{-1}) as the intermediate band in the spectrum of **6**, thus establishing that it is associated with the stretching vibration of the penterminal sp^2 C—H bond. In contrast, the wavenumbers of the other two bands associated with sp^2 C—H stretching vibrations of **6** are strongly affected by deuteriation. The corresponding bands in the spectrum of **6**-5,5-$^2H_2$ are at 2308 and 2215 cm^{-1} and are logically attributed to the asymmetric and symmetric stretching vibrations of the sp^2 C—D bonds of the deuteriated methylene group.

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Techniques used: Raman

Fig. 1–4: Raman spectra

Schemes: 4

References: 12

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‡The expression 'asymmetric' in this connection means that the vibration in question does not have a formal centre of symmetry.