Relationship of the ^{17}O Chemical Shift to the Stretching Frequency of the Hydroxy-group in Saturated Alcohols

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A good linear relationship was found to exist between the ^{17}O chemical shift and the OH stretching frequency of the hydroxy-group in some saturated alcohols. Similar relationships were also found between the ^{17}O chemical shifts for methyl ethers and anisoles and the OH stretching frequencies for the corresponding saturated alcohols and phenols. CNDO/2 Calculations were carried out to obtain the OH stretching frequency of the hydroxy-group and the local paramagnetic term of the oxygen atom for a series of methyl-substituted methanols. The results are compared with the experimental data.

THE OH stretching vibration band in saturated alcohols, R–OH, provides useful information not only on the nature of the substituent, R, but also on the molecular conformation.[1-5] The OH stretching frequency, ν_{OH}, has been reported to shift to a lower wavenumber when α-H is substituted by a methyl group, whereas it shifts to higher field when β-H is substituted.[3,4] After recent advances in n.m.r. spectroscopy, ^{17}O chemical shifts, $\delta^{17}O$, have been measured for a number of saturated alcohols. The ^{17}O chemical shift has been reported to shift to a lower magnetic field when α-H is substituted by a methyl group, but to higher field in the case of β-substitution.[6,7]

The behaviour of ν_{OH} strongly resembles that of $\delta^{17}O$ in regard to the additivities for the substitution shifts of R–OH. Regression analysis was thus carried out between the ν_{OH} and $\delta^{17}O$ values reported for 18 typical alcohols. The $\delta^{17}O$ values of aliphatic ethers have been reported to show behaviour similar to that of alcohols.[7,8] The analysis was also carried out for the ν_{OH} values of R–OH and the $\delta^{17}O$ values of the corresponding methyl ethers, R–OCH₃.

The ν_{OH} values for substituted phenols, XC_6H_4–OH, provides information on the electronic structures.[9,10] Katoh *et al.*[11] measured $\delta^{17}O$ for substituted anisoles, XC_6H_4–OCH₃, and found a good linear relationship between the $\delta^{17}O$ values and the π-electron densities at the oxygen atom of the methoxy-group calculated by the CNDO/2 method. Thus the analysis was also performed between ν_{OH} of XC_6H_4–OH and $\delta^{17}O$ of XC_6H_4–OCH₃. The two parameters shift, respectively, to lower wavenumber and magnetic field with decreasing π-electron density at the oxygen atom due to substituent effects.[9,11] On the other hand, the $\delta^{17}O$ values of R–OH and R–OCH₃ shift to lower magnetic fields with increasing electron density at the oxygen atom by substitution of an α-H by a methyl group.[7,8]

The ν_{OH} values of R–OH have been interpreted by invoking the three conformers (I)—(III) (Figure 2) and their relative populations, but not by means of the inductive effect.[2] However, we obtained similar relationships between $\delta^{17}O$ and ν_{OH} for both aliphatic and aromatic series. Therefore, in order to explain the experimental results theoretically, we carried out CNDO/2 calculations[12] for a series of methyl-substituted

methanols to obtain approximate values of ν_{OH} and the ^{17}O local paramagnetic term; the average excitation energy approximation[13] was used for the latter.

OH Stretching Frequency–^{17}O Chemical Shift Relationships.—When $\delta^{17}O$ values were plotted against ν_{OH} values selected from available literature data,[4,6,8,9,11] the linear relationships (A)—(C) (Figure 1) were found. ν_{OH}
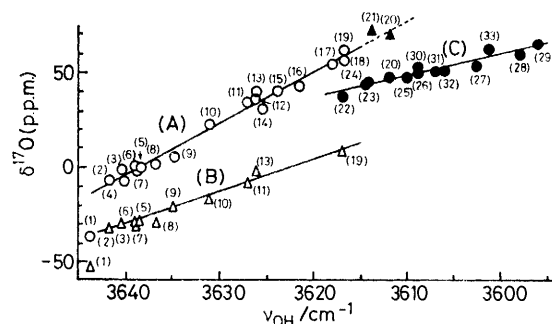

FIGURE 1 Plots of ^{17}O chemical shifts of R-OH (○),[6] R-OCH₃ (△),[8] XC_6H_4-OH (▲),[6] and XC_6H_4-OCH₃ (●)[11] *versus* free OH stretching frequencies of the corresponding R-OH[4] and XC_6H_4-OH.[9] Substituents: (1) R = CH₃; (2) R = (CH₃)₃-CCH₂; (3) R = (CH₃)₂CHCH₂; (4) R = CH₃CH₂(CH₃)-CHCH₂; (5) R = CH₃CH₂CH₂; (6) R = CH₃CH₂CH₂CH₂; (7) R = (CH₃)₂CHCH₂CH₂; (8) R = (CH₃)₃CCH₂CH₂; (9) R = CH₃CH₂; (10) R = (CH₃CH₂)₂CH; (11) R = CH₃CH₂-(CH₃)CH; (12) R = CH₃CH₂CH₂(CH₃)CH; (13) R = (CH₃)₂-CH; (14) R = cyclo-C₅H₉; (15) R = cyclo-C₆H₁₁; (16) R = (CH₃CH₂)₃C; (17) R = (CH₃CH₂)₂(CH₃)C; (18) R = CH₃CH₂-(CH₃)₂C; (19) R = (CH₃)₃C; (20) X = H; (21) X = o-CH₃; (22) X = p-OCH₃; (23) X = p-CH₃; (24) X = p-F; (25) X = p-Cl; (26) X = p-Br; (27) X = p-CF₃; (28) X = p-CN; (29) X = p-NO₂; (30) X = m-F; (31) X = m-Cl; (32) X = m-Br; (33) X = m-NO₂

is the OH stretching frequency (cm⁻¹) for R–OH and XC_6H_4–OH derivatives which are incapable of intra- and inter-molecular hydrogen bonding in CCl₄ solutions. In the present study, the ν_{OH} values of absorption maxima observed by van der Maas and Lutz[4] were used as approximations, although the frequency of the centre of the absorption should be adopted as ν_{OH} because the OH stretching vibration band arises from the conformers and their relative populations.[2,3] The OH stretching vibration bands of XC_6H_4–OH give symmetrical spectra and are shifted to lower wavenumbers with decreasing π-electron density at the oxygen atom of the hydroxy-group by the effect of the substituents, X.[9,10] $\delta^{17}O$ is the

^{17}O chemical shift (p.p.m. downfield from external H_2O) for R–OH, R–OCH$_3$, XC$_6$H$_4$–OH, and XC$_6$H$_4$–OCH$_3$.

The ^{17}O signals are shifted to lower magnetic field for XC$_6$H$_4$–OCH$_3$ as electron-withdrawing substituents are introduced into the benzene ring; this trend is the opposite of that for R–OH and R–OCH$_3$ mentioned above.[7,11] Nevertheless, in all the cases, the δ^{17}O and ν_{OH} values show linear correlations with negative slopes as shown by (A)—(C) in Figure 1. This point is discussed later on the basis of the CNDO/2 calculation.

The least-squares correlation equation for R–OH (2)—(19), represented by the regression line in Figure 1(A), is (1) with n 18 and r (correlation coefficient) 0.992. As

$$\delta^{17}O = -2.7316\nu_{OH} + 9\ 939.1 \tag{1}$$

shown in Figure 1, the ν_{OH} and δ^{17}O values for R–OH are shifted to lower wavenumber and magnetic field, respectively, by the β-effect on going from CH$_3$OH (1), through CH$_3$CH$_2$OH (9) and (CH$_3$)$_2$CHOH (13) to (CH$_3$)$_3$COH (19), but to higher ones with increasing γ-effect as seen on going from (9) to (2), from (13) to (10), and from (19) to (16). The least-sbuares equation for ν_{OH} of R–OH and δ^{17}O of the analogous R–OCH$_3$, shown in Figure 1(B), is (2) with n 11 and r 0.987. A

$$\delta^{17}O = -1.7705\nu_{OH} + 6\ 413.7 \tag{2}$$

simliar equation for the data for XC$_6$H$_4$–OCH$_3$ in Figure 1(C) is (3) with n 13 and r 0.960.

$$\delta^{17}O = -1.1531\nu_{OH} + 4\ 211.7 \tag{3}$$

Inspection of Figure 1 reveals that the δ^{17}O plots of C$_6$H$_5$OH (20) and o-CH$_3$C$_6$H$_4$OH (21) are located on line (A), while that of C$_6$H$_5$OCH$_3$ (20) deviates to lower magnetic field from line (B). The deviation may be attributed to the fact that because of conjugation between the benzene ring and the 2p non-bonding (n) electrons of the oxygen atom in the methoxy-group, its oxygen atom is subjected to less α-methyl effect than the oxygen atom of R–OCH$_3$ which have no conjugation. Equations (1)—(3) may prove useful for estimating δ^{17}O values for R–OH, R–OCH$_3$, XC$_6$H$_4$–OH, and XC$_6$H$_4$–OCH$_3$ from ν_{OH} data, which are much easier to observe than δ^{17}O values.

CNDO/2 Calculations.—The CNDO/2 calculations were carried out using the program of Pople and Beveridge.[12] From the available data [14] for analogous compounds, we adopted the geometries and co-ordinates of the model compounds, (1), (9), (13), and (19) shown in Table 1 and Figure 2, respectively. For compounds (9)

TABLE 1

Bond lengths and angles of molecules used in the CNDO/2 calculations

Geometry

R_{OH}/Å	0.96	$\widehat{COH}$ (°) 109
R_{CH}/Å	1.09	$\widehat{CCC} = \widehat{HCH} = \widehat{CCO}$ (°) 109.467
R_{CO}/Å	1.43	All torsion angles 60°
R_{CC}/Å	1.54	

and (13) which have two conformers, configurations (I) and (II) and (II) and (III) (Figure 2) were calculated, respectively. When an OH stretching force constant was calculated, the OH bond length was optimized in the direction of the OH axis, retaining the other parameters.

(a) OH *Stretching frequency.* The OH stretching vibration band, ν_{OH}, virtually corresponds to an OH stretching mode.[15] The normal mode for the ν_{OH} band can be assumed to be approximately equal to a pure OH stretching mode. Assuming a harmonic oscillator
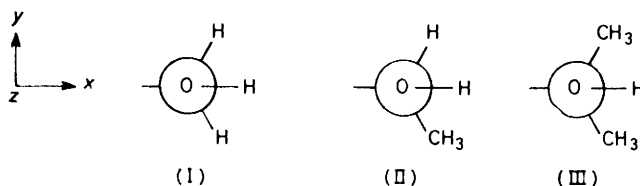

FIGURE 2   Co-ordinates of alcohol rotamers

model, the force constant, K, of the ν_{OH} band was calculated from the second derivative of change in total energy, E, with the variation in OH bond length (R_{OH}) near the optimum OH bond length, $R_{OH}°$, since the assumption gives equation (4) [12,16] where $K = \partial^2 E/\partial q^2$ and

$$E = Kq^2/2 \tag{4}$$

$q = R_{OH} - R_{OH}°$. The ν_{OH} value was calculated from the K value by the usual method. By partitioning E,[12] which has R_{OH} 0.96 Å, OH bond energies E_{OH} and $E'_{OH} = E_{OH} + \sum_n E_n$ were calculated as a measure of the strength of the OH bond, where $\sum_n E_n$ is the sum of non-bonding interaction energies between an OH group and other atoms in the molecule; note that we found the greater part of $\sum_n E_n$ was occupied by the repulsion energies for the oxygen atom of an OH group. The E_{OH}, E'_{OH}, $R_{OH}°$, K, and ν_{OH} values obtained from the CNDO/2 calculation are given in Table 2 together with the corresponding experimental ν_{OH} values. In general, the CNDO/2 calculations overestimate their values.[12,15,17] The absolute values for ν_{OH} are very large, but the shifts to lower wavenumbers with increasing number of β-methyl groups run closely parallel to the experimental ones. In addition, the $R_{OH}°$ value increases with decreasing K values. On the other hand, the change in the E_{OH} value, which increases with decreasing K values, as shown in Table 2, was the reverse of the predicted trend, although a change in the E'_{OH} value agreed completely with that predicted. This suggests theoretically that the non-bonding interaction is more important than the inductive one, which is caused by replacement of hydrogen by a methyl group, because the shift to lower wavenumbers of the ν_{OH} band corresponds approximately to a weakened OH bond due to the non-bonding interaction. This seems to conform to a concept of conformational heterogeneity.[1-3,18]

(b) ^{17}O *Local paramagnetic term.* The ^{17}O chemical shift is approximately governed by the local paramag-

TABLE 2

OH Bond energies,[a] optimum OH bond lengths, force constants, and frequencies for methyl-substituted methanols

No.	Compound	Type[b]	E_{OH}/a.u.	E'_{OH}[c]/a.u.	R_{OH}°/Å	K[d]/mdyn Å^{-1}	ν_{OH}^{cal}/cm^{-1}	ν_{OH}^{obs} [f]/cm^{-1}	$10^{-4}A_{OH}$ [g]/mol^{-1} l cm^{-2}
(1)	CH$_3$OH	I	−0.7411	−0.7186	1.0303	16.716	5 470.1	3 644.1	0.43
(9)	CH$_3$CH$_2$OH	I	−0.7409	−0.7145	1.0306	16.706	5 468.6	3 638.5	0.27
			(−0.7414)[e]	(−0.7145)[e]	(1.0306)[e]	(16.707)[e]	(5 468.7)[e]	(3 634.8)[e]	
		II	−0.7425	−0.7144	1.0305	16.708	5 468.8	3 627.8	0.14
(13)	(CH$_3$)$_2$CHOH	II	−0.7419	−0.7118	1.0309	16.693	5 466.3	3 627.7	0.27
			(−0.7425)[e]	(−0.7117)[e]	(1.0309)[e]	(16.690)[e]	(5 465.8)[e]	(3 623.5)[e]	
		III	−0.7437	−0.7116	1.0308	16.683	5 464.7	3 615.5	0.14
(19)	(CH$_3$)$_3$COH	III	−0.7428	−0.7105	1.0312	16.672	5 463.0	3 617.2	

[a] R_{OH} = 0.96 Å. [b] Ref. 2. [c] $E'_{OH} = E_{OH} + \Sigma E_n$, where E_n is the non-bonding interaction energy for the OH group. [d] Calculated using least-squares quadratic fit using five points taken at 0.01 Å intervals of R_{OH} around the energy minimum. [e] The values were estimated using integrated intensity ratios of the ν_{OH} band for rotamers. [f] All determined in CCl$_4$ at a concentration of ca. 0.005M. [g] Integrated intensity was calculated using Ramsay's method.[22]

netic term for the oxygen atom.[19] According to Pople's theory,[13] the zz-component of the local paramagnetic contribution is given by equation (5) where $\langle r^{-3}\rangle_{2p}$ is

$$(\sigma_p^{AA})_{zz} = -\frac{e^2\hbar^2}{2m^2c^2(\Delta E)}\langle r^{-3}\rangle_{2p} \times$$
$$[(Q_{AA})_{zz} + \sum_{B\neq A}(Q_{AB})_{zz}] \quad (5)$$

$$(Q_{AA})_{zz} = 2 - 2(P_{x_Ax_A} - 1)(P_{y_Ay_A} - 1) + 2P_{x_Ay_A}^2 \quad (6)$$

$$(Q_{AB})_{zz} = -2P_{x_Ax_B}P_{y_Ay_B} + 2P_{x_Ay_B}P_{y_Ax_B} \quad (7)$$

the mean inverse cube radius for the oxygen 2_p orbitals, ΔE is the average electronic excitation energy, and $P_{\mu\nu}$ are elements of the charge density and bond order matrix. The $\langle r^{-3}\rangle_{2p}$ value is evaluated by equation (8).

$$\langle r^{-3}\rangle_{2p} = \frac{1}{24}(Z_{2p}/a_0)^3 \quad (8)$$

According to Slater's rules,[20] Z_{2p} of the oxygen atom is given by equation (9) where q^{net} is the net charge on the oxygen atom.

$$Z_{2p} = 4.55 + 0.35q^{net} \quad (9)$$

The lower field shifts due to the β-methyl effect in alcohols and ethers have been reported[7] to parallel the decrease in their ionization potentials. Therefore, applying Koopmans' theorem,[21] the ΔE value in equation (5) is assumed to be the negative of the highest occupied orbital energy, ε_{HOMO}. The calculated results for σ_p^{av} are given in Table 3, together with the observed values of $\delta^{17}O$.[6]

The increase in the absolute value of the paramagnetic term, σ_p^{av}, due to the β-methyl effect for the model compounds is consistent with the increase in the lower field shift in the ^{17}O chemical shift. However, the $\langle r^{-3}\rangle_{2p}$ and $1/3\sum_i[(Q_{AA})_{ii} + \sum_{B\neq A}(Q_{AB})_{ii}]$ contributions to the σ_p^{av} decrease on going from compound (1) through (9) and (13), to (19), and their values are inversely proportional to the negative value of the σ_p^{av}.

The calculation suggests that the σ_p^{av} is primarily governed by the ΔE in this case, as pointed out experimentally by Sugawara et al.[7] However, in anisoles the $\langle r^{-3}\rangle_{2p}$ and $[(Q_{AA})_{ii} + \sum_{B\neq A}(Q_{AB})_{ii}]$ have been reported to be the main contribution to the ^{17}O local paramagnetic term, σ_p.[11] A linear relationship with a positive slope in XC$_6$H$_4$–OCH$_3$ has been reported[11] for a plot of $\delta^{17}O$ versus Hammett σ^- constants which reflect changes in electron density at the oxygen atom, but the trend for

TABLE 3

Calculated ^{17}O local paramagnetic terms,[a] σ_p, and observed ^{17}O chemical shifts, $\delta^{17}O$, for methyl-substituted methanols

No.	Compound	Type[b]	P_{AA}[c]	$10^{-24}\langle r^{-3}\rangle_{2p}$/cm^{-3}	ε_{HOMO}/a.u.	ii[d]	$(Q_{AA})_{ii} + \Sigma(Q_{AB})_{ii}$	$(\sigma_p^{AA})_{ii}$ (p.p.m.)	σ_p^{av} [e] (p.p.m.)	$\delta^{17}O$ [g] (p.p.m.)
(1) CH$_3$OH		I	6.2464	25.0096	−0.5704	xx	1.6848	−291.5	−291.9	−37.0
						yy	2.0704	−358.2		
						zz	1.3070	−226.1		
(9) CH$_3$CH$_2$OH		I	6.2548	24.9599	−0.5469	xx	1.6743	−301.5	−302.0	
						yy	2.0412	−367.5		
						zz	1.3172	−237.2		
									(−300.7) [f]	5.9
		II	6.2588	24.9368	−0.5506	xx	1.6379	−292.6	−298.1	
						yy	2.0552	−367.2		
						zz	1.3122	−234.4		
(13) (CH$_3$)$_2$CHOH		II	6.2654	24.8978	−0.5301	xx	1.6314	−302.3	−307.7	
						yy	2.0305	−376.2		
						zz	1.3207	−244.7		
									(−307.2) [f]	39.8
		III	6.2687	24.8783	−0.5295	xx	1.6002	−296.6	−306.2	
						yy	2.0410	−378.3		
						zz	1.3154	−243.8		
(19) (CH$_3$)$_3$COH		III	6.2743	24.8459	−0.5128	xx	1.5962	−305.1	−314.7	62.3
						yy	2.0199	−386.1		
						zz	1.3224	−252.8		

[a] R_{OH} = 0.96 Å. [b] Ref. 2. [c] P_{AA} is charge density on the oxygen atom. [d] i is either x, y, or z. [e] $\sigma_p^{av} = 1/3[(\sigma_p^{AA})_{xx} + (\sigma_p^{AA})_{yy} + (\sigma_p^{AA})_{zz}]$. [f] The values were estimated using integrated intensity ratios of the ν_{OH} band for rotamers. [g] Ref. 6.

the plot of $\delta^{17}O$ *versus* Taft σ^* constants in R–OH and R–OCH$_3$ is just the opposite. This may be largely due to the difference in the main contribution to σ_p described above.

(c) *Calculated* ν_{OH}–σ_p^{av} *relationship*. For empirical correlations, we have equations (1)—(3) as experimental results. Although the presence of some relationships between ν_{OH} and $\delta^{17}O$ might be expected, we have no straightforward proof that this relationship should be linear. When the calculated σ_p^{av} values shown in Table 3 were plotted against the calculated ν_{OH} shown in Table 2 for the series of substituted methanols, a linear relationship was found as shown in Figure 3. It follows
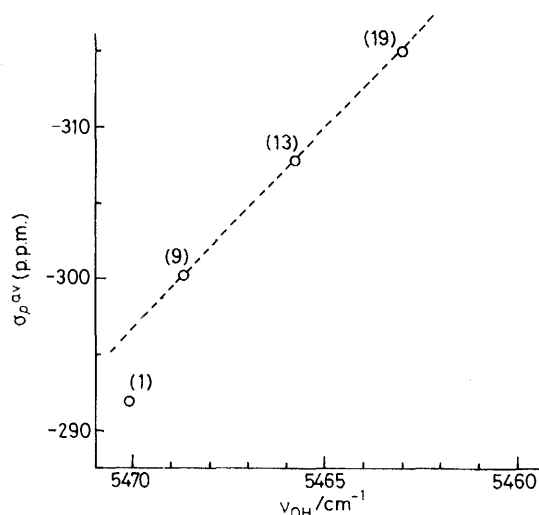

FIGURE 3   Plots of σ_p^{av} *versus* ν_{OH} from CNDO/2 calculation

that a linear relationship can be obtained theoretically between these values; this may be due to the fact that in the model compounds, the increase in the non-bonding interaction to the oxygen atom is proportional to the increase in instability of the highest occupied orbital which is mainly occupied by the lone-pair electrons of the oxygen atom. It is interesting to note that the methanol plot deviates to higher magnetic field for both experimental and theoretical correlations as shown in Figures 1 and 3, respectively.

In summary, the present study provides the following conclusions: (a) linear relationships between ν_{OH} and $\delta^{17}O$ exist for the compounds studied, (b) CNDO/2 calculation affords a linear relationship between these

values for simple substituted methanols, and (c) the β-methyl effect on the calculated ν_{OH} and σ_p^{av} values in the present case is rationalized approximately by the non-bonding interaction and the average electron excitation energy, respectively.

EXPERIMENTAL

Calculations were performed on a FACOM M140 computer. I.r. spectra were measured on a JASCO DS-403G grating spectrometer calibrated in the usual manner.

REFERENCES

[1] R. Piccolini and S. Winstein, *Tetrahedron Lett.*, 1959, 4.
[2] M. Oki and H. Iwamura, *Bull. Chem. Soc. Jpn.*, 1959, **32**, 950.
[3] L. Joris, P. von R. Schleyer, and E. Ōsawa, *Tetrahedron*, 1968, **24**, 4759.
[4] J. H. van der Maas and E. T. G. Lutz, *Spectrochim. Acta*, 1974, **30A**, 1974.
[5] M. Takasuka and H. Tanida, *J. Chem. Soc., Perkin Trans. 2*, 1980, 486.
[6] J. K. Crandall and M. A. Centeno, *J. Org. Chem.*, 1979, **44**, 1183.
[7] (a) T. Sugawara, Y. Kawada, M. Katoh, and H. Iwamura, *Bull. Chem. Soc. Jpn.*, 1979, **52**, 3391; (b) T. Sugawara, Y. Kawada, and H. Iwamura, *Chem. Lett.*, 1978, 1371.
[8] C. Delseth and J. P. Kintzinger, *Helv. Chim. Acta*, 1978, **61**, 1321.
[9] C. Laurence and M. Berthelot, *Spectrochim. Acta*, 1978, **34A**, 1127.
[10] L. A. Cohen and W. M. Jones, *J. Am. Chem. Soc.*, 1963, **85**, 3404.
[11] M. Katoh, T. Sugawara, Y. Kawada, and H. Iwamura, *Bull. Chem. Soc. Jpn.*, 1979, **52**, 3475.
[12] J. A. Pople and D. L. Beveridge, 'Approximate Molecular Orbital Theory,' McGraw–Hill, New York, 1970.
[13] J. A. Pople, (a) *Faraday Discuss. Chem. Soc.*, 1962, **34**, 7; (b) *J. Chem. Phys.*, 1962, **37**, 53; (c) *ibid.*, p. 60; (d) *Mol. Phys.*, 1962—1963, **7**, 301.
[14] (a) M. Kimura and M. Kubo, *J. Chem. Phys.*, 1959, **30**, 151; (b) J. D. Swalen, *ibid.*, 1955, **23**. 1739; (c) M. Kimura, *J. Chem. Soc. Jpn.*, 1950, **71**, 18; (d) M. Yamada, *Bull. Chem. Soc. Jpn.*, 1954, **27**, 170.
[15] M. Takasuka and Y. Matsui, *J. Chem. Soc., Perkin Trans. 2*, 1979, 1743.
[16] E. B. Wilson, jun., J. C. Decius, and P. C. Cross, ' Molecular Vibrations,' McGraw–Hill, New York, 1955.
[17] G. A. Segal, *J. Chem. Phys.*, 1967, **47**, 1876.
[18] E. T. G. Lutz and J. H. van der Maas, *Spectrochim. Acta*, 1978, **34A**, 915.
[19] K. A. K. Ebraheem and G. A. Webb, *Prog. Nucl. Magn. Reson. Spectrosc.*, 1977, **11**, 149.
[20] J. C. Slater, *Phys. Rev.*, 1930, **36**, 57.
[21] T. Koopmans, *Physica*, 1933, **1**, 104.
[22] D. A. Ramsay, *J. Am. Chem. Soc.*, 1952, **74**, 72.