Individual CH Bond Strengths in Simple Organic Compounds: Effects of Conformation and Substitution

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1 Introduction: 'Isolated' CH Stretching Frequencies, $\nu(\mathrm{CH})^{\mathrm{is}}$

The purpose of this article is to review the recent evidence for the strengths of individual CH bonds which has been obtained from a study of CH stretching frequencies in incompletely deuteriated compounds, and to discuss its implications in the fields of molecular geometry, chemical kinetics, bonding theory, and substituent effects.

The data obtained indicate the strength of the CH bond in its *equilibrium* state, as does the bond length, in contrast to the dissociation energy D°_{298}, which measures the *difference* between the energy of the equilibrium state, and that of its dissociated products. As will be seen later, these two kinds of 'bond strength' are often, though not always, related.

The data are largely new, and precise to an extent rarely possible from conventional studies of CH stretching frequencies of normal, undeuteriated species. In the latter, the vibrational spectrum is highly complicated, mainly due on the one hand, to effects of coupling between CH bonds in CH_3 and CH_2 groups to give symmetric and antisymmetric stretching modes, and on the other, to Fermi resonances between these and overtones of CH_3 and CH_2 bending modes. These difficulties are almost always removed by the observation of CH stretching frequencies in which all hydrogens are deuteriated except for one. For example in a methyl compound, the CHD_2 derivative is studied. In such compounds the CH bending modes are much lower than in the CH_3 one, and Fermi resonances become insignificant in the CH stretching region. Moreover the coupling to other motions of the CH stretching is minimal, probably amounting to less than 10 cm^{-1} in $\nu(\mathrm{CH})$. Such frequencies have been termed 'isolated' ones, [symbol $\nu(\mathrm{CH})^{\mathrm{is}}$].[1] While they may be used to calculate individual CH bond stretching force constants, the *variation* in coupling to other motions is so small, probably less than 5 cm^{-1} in $\nu(\mathrm{CH})$,[2] that the $\nu(\mathrm{CH})^{\mathrm{is}}$ values may be used directly as a measure of strength.

One of the most pleasing results of CHD_2 substitution in a methyl compound is the demonstration of the presence of more than one type of CH bond, in that

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[1] D. C. McKean, *Spectrochim. Acta*, 1975, **31A**, 861.

[2] D. C. McKean, *Spectrochim. Acta*, 1973, **29A**, 1559.

group, from a single spectrum. This was first carried out by Saur, Lavalley, and Romanet in CH_3CH_2X compounds, where X was Cl, Br, or COOH.[3] The potential barrier opposing internal rotation of the CH_3 group is sufficiently high that a solitary CH bond in a CHD_2 group produces two conformers, one in which the hydrogen is *trans* to a CH bond in the CH_2 group, the other in which it is *trans* to the CX bond. The barrier is of course low enough to ensure that both conformers are always present. Two bands are then seen in the i.r. spectrum.* In the spectrum of $(CHD_2)_2NH$[4] three i.r. bands are seen, as in Figure 1. Here the solitary CH bond can be *trans* either to H, or to the other methyl group, or to the lone pair of electrons.†

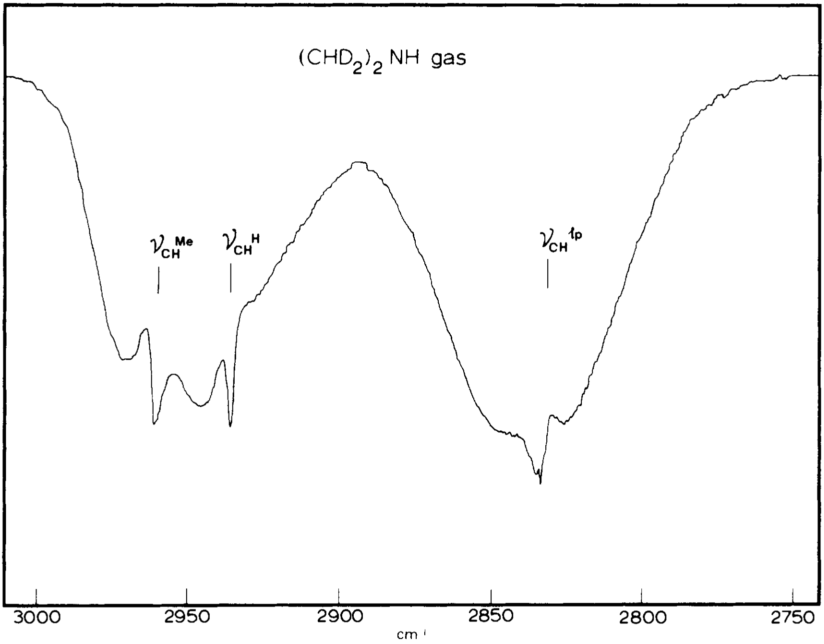

Figure 1 *Infrared spectrum in gas phase of* $(CHD_2)_2NH$.[35] CH^X *signifies the CH bond* trans *to group X*

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*The success of this experiment depends on the short time scale of the i.r. absorption process. The longer time scale required for the n.m.r. experiment means that only an average signal from both kinds of proton is observed in the latter.

†The spectrum is *not* complicated by the presence of *two* CHD_2 groups. Coupling between two CH bonds separated by another atom such as C, N, or O has been shown to be negligible.[4]

[3] O. Saur, J. C. Lavalley, and R. Romanet, *Compt. rend.*, 1969, **269**, *B*, 816.

[4] D. C. McKean, *Chem. Comm.*, 1971, 1373.

The first appreciation of the quantitative value of such CHD_2 frequencies appears to have been made by Allan and McKean, in a study of $(CHD_2)_2O$.[5] The foundation for the use of CH stretching frequencies for the prediction of bond lengths and dissociation energies, however, was laid in 1962 by Bernstein,[6] who correlated 'average' stretching frequencies for CH_3, CH_2, and CH groups with bond length and dissociation energy, respectively. These 'average' ν(CH) data however are only physically meaningful if all the CH bonds in the one group are identical, and even then they are subject to error due to Fermi resonances, being derived from frequencies of the normal, undeuteriated species.

2 The Quantitative Use of $\nu(CH)^{is}$ Values

A. $\nu(CH)^{is}$ Values and Predictions of Molecular Geometry.—$\nu(CH)^{is}$ values may be used generally for the prediction of CH bond lengths, and, in the case of certain CH_3 groups, for the prediction of HCH angles. For bond lengths, the correlation curve of Figure 2 is employed.[7] The experimental bond lengths are confined to spectroscopic r_o or r_s values, for maximum compatibility.* Between 3050 and 2800 cm^{-1}, the data are well fitted by the equation $r_o(\text{Å}) = 1.402 - 0.000\,103\,5\nu(CH)^{is}$.

Two pairs of points, those for Me_2O and Me_3N, are particularly pleasing, since in each compound both the i.r. $\nu(CH)^{is}$ bands and the microwave structures indicate the presence of two types of CH bond, the resulting pair of points lying close to the correlation curve.

Another encouraging feature has been the number of occasions on which improvement in the precision or in the interpretation of a microwave spectrum has resulted in moving a point much nearer the curve, *e.g.* for HCNO,[8] CH_3CN,[9] $CH_3C{\equiv}CH$,[10] and CH_3F.[11] Two notable anomalies remain, however, as previously noticed by Bernstein, *viz.* CHF_3 and $CHCl_3$. For these the microwave CH bond lengths are greater by 0.014 Å and by 0.015 Å than those predicted from ν(CH).† Apart from these, one can predict bond length differences with an accuracy of about ±0.0005 Å, since the slope of the curve is approximately 10 cm^{-1} per 0.001 Å, and the uncertainty in $\nu(CH)^{is}$ is less than 5 cm^{-1} (due mainly to variations in coupling, not to experimental inaccuracy). This accuracy of

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*In the original plot, 0.003 Å was added to each r_s value, as for some molecules there is reason to suppose $r_o \gtrsim r_s + 0.003$ Å. In olefinic CH bonds, however, there is little evidence to support this.

†Assuming $r_o = r_s + 0.003$. A smaller discrepancy of 0.009 Å, possibly having the same origin, occurs in Me_3CH, for the tertiary CH bond.[12]

[5] A. Allan and D. C. McKean, 'International Congress on Molecular Spectroscopy', Liège 1969; A. Allan, D. C. McKean, J. P. Perchard, and M. L. Josien, *Spectrochim. Acta.*, 1971, **27A**, 1409.

[6] H. J. Bernstein, *Spectrochim. Acta*, 1962, **18**, 161.

[7] D. C. McKean, J. L. Duncan, and L. Batt, *Spectrochim. Acta*, 1973, **29A**, 1037.

[8] B. P. and M. Winnewisser, and F. Winther, *J. Mol. Spectroscopy*, 1974, **51**, 65.

[9] J. L. Duncan, D. C. McKean, and N. D. Michie, *J. Mol. Structure*, 1974, **21**, 405.

[10] J. L. Duncan, D. C. McKean, P. D. Mallinson, and R. D. McCulloch, *J. Mol. Spectroscopy*, 1973, **46**, 232.

[11] D. F. Eggers, *J. Mol. Structure*, 1976, **31**, 367.

[12] D. C. McKean, S. Biedermann, and H. Bürger, *Spectrochim. Acta*, 1974, **30A**, 845.

±0.0005 Å greatly exceeds the precision of most microwave determinations. It has therefore been of considerable interest to discover that *ab initio* calculations, aided by the force method of Pulay for optimizing geometry,[13] reproduce many of the CH bond length *variations* to 0.001 Å or better. Table 1 shows some recent

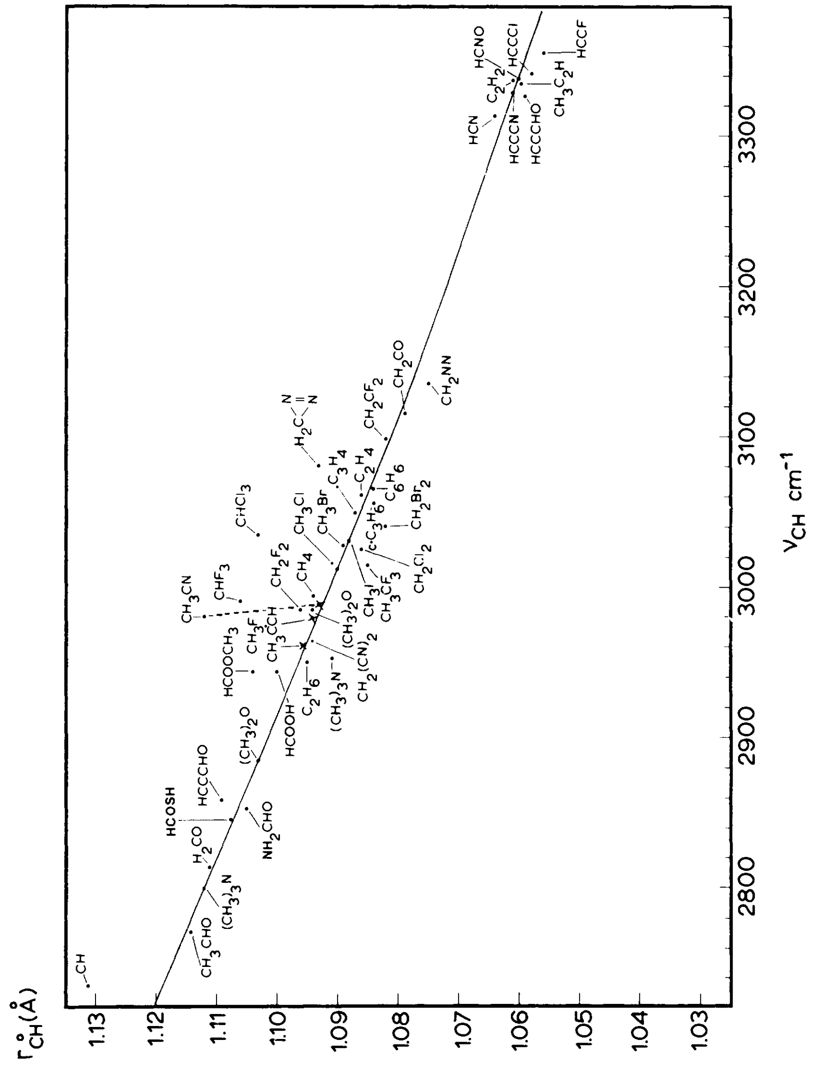

Figure 2 *Correlation between* ν(CH)^{is} *and* r_0(CH).[7] *The dotted line for* CH_3CN *shows the improvement due to a recent redetermination of geometry*[9]

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[13] P. Pulay, *Mol. Phys.*, 1969, **17**, 197.

Table 1 $\nu(CH)^{is}$ *and predictions of* r_0, D°_{298} *in some hydrocarbons*

		$\nu(CH)^{is}/cm^{-1}$	$r_0(pred.)/Å$	$r_e(4\text{—}31G)/Å$	$r_0 - r_e/Å$	$D^\circ_{298}(pred.)/kcal\ mol^{-1}$	$D^\circ_{298}(obs.)/kcal\ mol^{-1}$
CH_4		2992[a]	1.092	1.081[b]	0.011	103.2	104.0[a]
C_2H_6		2950[a]	1.096(5)	1.083[b]	0.013(5)	99.6	98[a]
$(CH_3)_2CH_2$	s—H	2920[c]	1.099(5)	1.085[b]	0.014(5)	97.0	95[a]
	p—H^{Me}	2950[c]	1.096(5)	1.083[b]	0.013(5)	99.6	
	p—H^{H}	2936[c]	1.098	1.084[b]	0.014	98.4	98[a]
$(CH_3)_3CH$	t—H	2894[c]	1.102(5)			94.8	92[a]
	p—H^{Me}	2943[c]	1.097			99.0	
	p—H^{H}	2924[c]	1.099			97.3	
$(CH_3)_4C$		2934[a]	1.098			98.2	99.3[a]
$PhCH_3$	Me	2947[d]	1.097			99.4	88.3[a]
cyclo—C_3H_6		3056[a]	1.085(5)	1.072[b]	0.013(5)	108.7	100.4[a]
cyclo—C_4H_8		2956[a]	1.096			100.1	96.8[a]
C_2H_4		3055[e]	1.085(5)	1.073[b]	0.012(5)	108.7	108[a]
$CH_3CH{=}CH_2$							
	H_α	3013[f]	1.090	1.076[b]	0.014	105.0	
	H_t	3064[f]	1.084(5)	1.072[b]	0.012(5)	109.4	
	H_c	3039[f]	1.087	1.074[b]	0.013	107.3	
$(CH_3)_2C{=}CH_2$		3050[f]	1.086			108.2	
$CH_2{=}C{=}CH_2$		3049[a]	1.086			108.1	
C_6H_6		3065[a]	1.084(5)			109.5	110.5[a]
C_2H_2		3336[a]	1.060	1.051[b]	0.009		128[a]
CH_3—CCH	ac—H	3334[a]	1.060	1.050[g]	0.010	~128	
	Me—H	2958[a]	1.095(5)	1.083[g]	0.013	100.3	93.9[h]

[a]ref. 7; [b]refs. 21, 22*a*; [c]ref. 12; [d]J. Lascombe, personal communication; see also text, Section 3G; [e]ref. 23; [f]ref. 1; [g]ref. 24; [h]ref. 25; p = primary. s = secondary, t = tertiary, ac = acetylenic, $H_{\alpha,t,c}$ = hydrogen α, *trans*, or *cis* to methyl, H^X = H *trans* to X. For data for Me in propene, but-1-ene see Section 3F.

examples of this amongst hydrocarbons, other examples being found in other tables. It may be concluded that a very simple i.r. experiment yields at least one geometric parameter, r°_{CH}, more accurately than any other known method.

The correlation between $\nu(CH)^{is}$ and the HCH angle for methyl groups is shown in Figure 3.[14] For the line drawn, $\alpha^{\circ}_{HCH} = 0.0471\nu(CH)^{is} - 31.1$. It appears to hold for symmetric CH_3 groups, excluding CH_3F, and also, rather well, for CH_3XY_2 type compounds in which internal rotation is essentially free. For these last, the *average* $\nu(CH)^{is}$ frequency is used (see further, below). For asymmetric CH_3 groups it enables a rough estimate to be made of *average* HCH angles, except where CH_3N or CH_3O are present. One success of the correlation was the prediction of 107.0° for the HCH angle in Me_4C. A recent experimental determination yields 106.6° for this quantity.[15] No such correlation exists for HCH angles in methylene groups in general, but a rough one for $C{=}CH_2$ systems is evident in the data compiled by Duncan.[16] It is not linear.

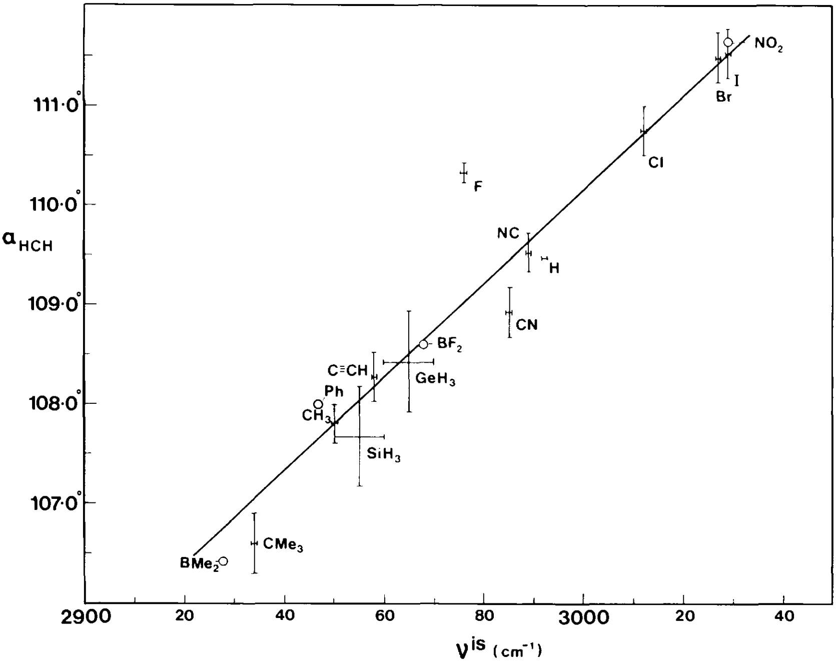

Figure 3 *Correlation between* $\nu(CH)^{is}$ *and* αHCH *in symmetric* CH_3 *groups (points denoted* ┼*). Points denoted* ○ *are for asymmetric methyl groups which undergo free internal rotation, using* $\nu(CH)^{av.is} = \frac{1}{2}[\nu(CH)_{\parallel} + \nu(CH)_{\perp}]$ *(no error indicated)*

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[14] D. C. McKean, *J. Mol. Structure*, 1976, **34**, 181.

[15] L. S. Bartell and W. F. Bradford, *J. Mol. Structure*, 1977, **37**, 113.

[16] J. L. Duncan, *Spectrochim. Acta*, 1970, **26A**, 429.

B. $\nu(CH)^{is}$ Values and Predictions of Dissociation Energies: Applications in Chemical Kinetics.—Predictions of D°_{298} for the CH bond may be made using the correlation curve of Figure 4, based on experimental D°_{298} values, for the most

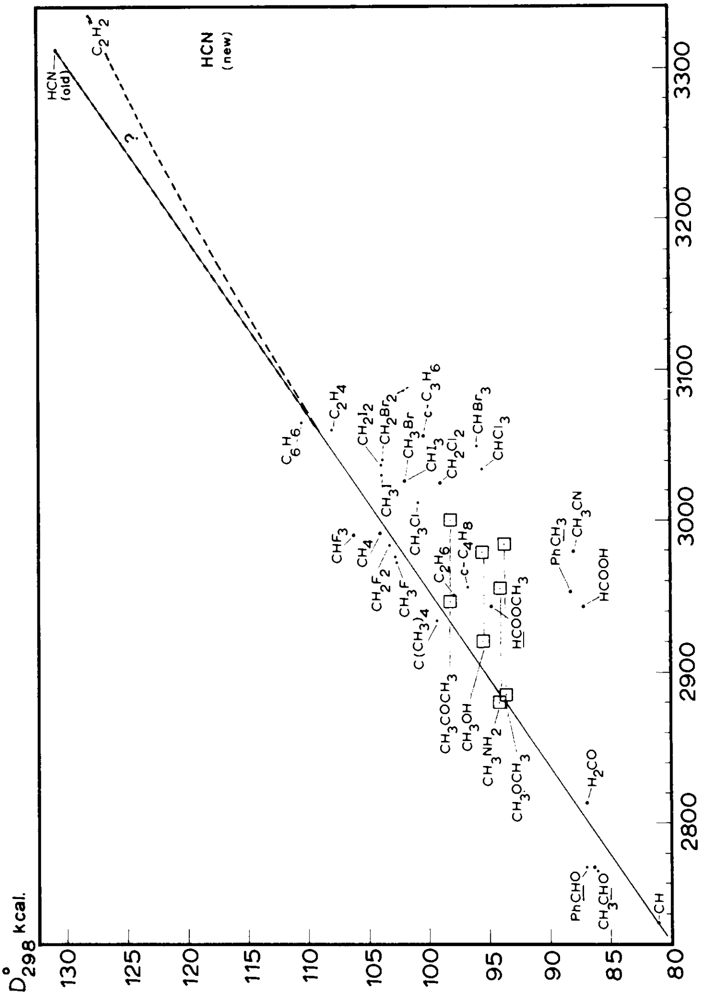

Figure 4 *Correlation between* $\nu(CH)^{is}$ *and dissociation energy,* D°_{298}, *in* kcal mol^{-1}.[7] *The newer experimental* D° *value of* 119.2 *for* HCN[17] *clearly conflicts with that for* C_2H_2 *and with the general trend of the lower points*

part derived from kinetic measurements.[7] The curve is drawn so as to lie close to points for compounds such as hydrocarbons which are likely to dissociate into radicals in which stabilization energy is negligible. Between 2700 and 3100 cm^{-1}, D°_{298} (kcal) = $0.08616\nu(CH)^{is} - 154.6$. The upper end of the curve was originally fixed by an earlier experimental D° value for HCN of 130.8 kcal mol^{-1}. This is now thought to be somewhat lower, at 119 kcal,[17] which may indicate that a little curvature is needed at the upper end of the plot. All the deviant points lie below the plot, the lowest being those in which stabilization energy, accompanied by marked change in geometry, has long been associated with the radical formed, *e.g.* $\cdot CH_2CN$, $\cdot CH_2Ph$. For each of four compounds, $(CH_3)_2CO$, CH_3OH, CH_3NH_2, and $(CH_3)_2O$, two points are plotted, thus □—□. This is because they each have two $\nu(CH)^{is}$ values, but only one experimental D°_{298} value. It may be significant that the point for the lower $\nu(CH)^{is}$ value in each case lies closer to the correlation curve, which is understandable if in the dissociation process it is only the weaker CH bond in the methyl group which is broken. The relevance of this to kinetic processes in which the rate-determining step is the breaking of a CH bond, seems obvious. The gradient of the curve, approximately 0.9 kcal mol^{-1} per 10 cm^{-1}, implies that in the same methyl group, differences in dissociation energy, and therefore of activation energy, of the order of 3—5 kcal mol^{-1} are common, and for CH_3—O and CH_3—N compounds are much greater, the highest difference found being 13 kcal mol^{-1} in trimethylamine. These differences are quite large enough to imply that only the weaker bond stands a chance of being broken in the kinetic process. This conclusion of course assumes an 'adiabatic' process in which the conformation of the methyl group is maintained, and that no stabilization energy is involved. It may be argued that the dissociation process should be considered to involve some kind of averaging of the separate strengths of the bonds in an asymmetric methyl group, particularly if internal rotation is essentially free. Against this, it must be stated firstly that there is clear evidence (see Section 3G) that CH bond strengths vary during a free internal rotation, secondly that in any event free rotation in the transition state seems highly unlikely, and thirdly that in a bimolecular breaking of the bond, the conformation of the CH bond, relative to the framework which causes the asymmetry, will probably be determined by the incoming trajectory of the colliding species. Thus for CH_3NO_2, it should be much easier for a radical to remove a hydrogen atom if it impinges at right angles to the skeleton plane, than if it strikes within that plane.* Both activation energy and pre-exponential factors should therefore be affected. What will happen in a unimolecular dissociation is harder to imagine, but it would be surprising if the fact that a CH bond may more easily be broken in one direction than in others does not play some part.

Stabilization Energy. The correlation plot of Figure 4 offers an improved means of measuring this quantity, as the difference between the D°_{298} value predicted

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*In addition to the predicted difference in D°_{298} of 5 kcal mol^{-1} (Section 3B). stabilization energy should further lower the activation energy for the approach at right angles.

[17] V. H. Dibeler and S. K. Liston, *J. Chem. Phys.*, 1968, **48**, 4765.

from the $\nu(CH)^{is}$ and the experimental one. One such application throws light on an old controversy, whether the weakness of a tertiary CH bond is due to a large stabilization energy of the t-butyl radical. The data in Table 1 indicate that the latter cannot exceed 2—3 kcal mol^{-1}. The tertiary CH bond is weak in the *equilibrium* state.

By contrast, halogenated methanes, other than fluorides, appear to involve significant amounts of stabilization energy. This may help to explain why the attack of chlorine atoms on ethyl chloride occurs almost wholly on the CH_2 group,[18] where the bonds have a D°_{298} of 102.5 kcal mol^{-1}, in contrast to the weaker bond in the CH_3 group which has a D°_{298} value of only 99.2 kcal mol^{-1}.[19]*

We note finally that the stabilization energy of 8 kcal mol^{-1} for the cyclo-$C_3H_5\cdot$ radical indicated by the present results seems rather high, and possibly the existing experimental value of D°_{298} is in error.[21–25]

C. $\nu(CH)^{is}$ Values and Force Constant Calculations.—It must be stated categorically that $\nu(CH)^{is}$ values should be the sole sources of *individual* bond stretching force constants, unless there is greater error in them, due to Fermi resonances in the partially deuteriated species, than there is in the normal, undeuteriated ones. The latter should normally be used only to determine stretching interaction force constants and/or Fermi resonance shifts.[2,26] This approach has been very seldom adopted, except in the treatment of vibrations of CH_3 or CH_2 groups which consider only CH or CD stretching (*e.g.* refs. 1, 2, and 12). It is of course easy to calculate $f(CH)$ in the diatomic approximation.† Such constants should normally be higher than those from a complete treatment by about 0.03 mdyn $Å^{-1}$.‡

In one comprehensive treatment of CH stretching frequencies,[28] $\nu(CH)^{is}$ values

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*That the CH dissociation energy can be important in hydrogen abstraction reactions is suggested by the preferential attack of Cl on the CH_2 α to O in ethers,[20] which is easily understood on the basis of the lone pair *trans* effect (see Section 3A).

†$f(CH)^{diat.} = [\nu(CH)^{is}/1302.83]^2/1.0756$. Normally variations in $f(CH)^{diat.}$ larger than 0.015 mdyn$Å^{-1}$ should be significant.

‡In H_2CO, however, owing probably to the abnormally high CH/CO stretch-stretch interaction,[27] $f(CH)^{diat.} < f(CH)$(g.f.f.).

[18] D. C. McKean and B. W. Laurie, *J. Mol. Structure*, 1975, **27**, 317; see also F. F. Rust and W. E. Vaughan, *J. Org. Chem.*, 1941, **6**, 479.

[19] D. C. McKean, O. Saur, J. Travert, and J. C. Lavalley, *Spectrochim. Acta*, 1975, **31A**, 1713.

[20] H. Singh and J. M. Tedder, *J. Chem. Soc (B)*, 1966, 612.

[21] R. Ditchfield, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, 1971, **54**, 724.

[22] (*a*) C. E. Blom, P. J. Slingerland, and C. Altona, *Mol. Phys.*, 1976, **31**, 1359; (*b*) C. E. Blom, L. P. Otto, and C. Altona, *Mol. Phys.*, 1976, **32**, 1137.

[23] J. L. Duncan, personal communication.

[24] D. C. McKean, unpublished work.

[25] R. Walsh, *Trans. Faraday Soc.*, 1971, **67**, 2085.

[26] (*a*) D. C. McKean, J. C. Lavalley, O. Saur, and J. Travert, *Spectrochim. Acta*, 1977, **33A**, 865; (*b*) D. C. McKean, J. C. Lavalley, O. Saur, H. G. M. Edwards, and V. Fawcett, *Spectrochim, Acta*, 1977, **33A**, 913.

[27] J. L. Duncan and P. D. Mallinson, *Chem. Phys. Letters*, 1973, **23**, 597.

[28] (*a*) H. Perrin, A. Cossée-Barbi, N. Brigot, and S. Odiot, *Mol. Phys.*, 1975, **29**, 1261; (*b*) H. Perrin, *J. Mol. Structure*, 1975, **28**, 305; (*c*) A. Cossée-Barbi and H. Perrin. *J. Mol. Structure*, 1976, **30**, 69.

have been used in several cases and differences here from 'diatomic' f(CH) values of the order of 0.07 mdyn Å^{-1} found. It is not clear however in this work, what assumptions were made concerning CH stretching interaction constants. These are in general very hard to determine.

The same work is notable for a CNDO treatment of CH stretching force constants. While CNDO calculations alone do not produce meaningful values of force constants, or of bond lengths, they can be made to predict variations in f(CH) on a semi-empirical basis with a substantial degree of success, although CH bonds affected by lone pair *trans* effects require a different approach to those in hydrocarbons.

3 Effects of Conformation and Substitution

These will be considered in seven groups:

A. the *trans* effect of lone pairs of electrons;
B. the systems H—C=O and H—C=N;
C. α-substitution effects of Me, halogens, CF_3, and CCl_3 in saturated compounds;
D. β-substitution effects of Me and halogens in saturated compounds;
E. substituent effects on olefinic CH bonds;
F. methyl groups adjacent to multiple bonds: hyperconjugation;
G. methyl groups attached to planar XY_2 skeletons.

Where substitution of a group X for hydrogen may be studied, one can define a substituent effect S^X as the difference in $\nu(CH)^{is}$ caused by that substitution. The evidence below suggests that it is rarely profitable to do this, in view of the non-additivity of such parameters.

A. The *trans* effect of lone pairs.—The presence of two types of CH bond in CH_3O or CH_2O compounds was first recognized by Freymann[29] in studies of the overtone region of ν(CH). The specific role of the lone pair was identified through the disappearance of the weak CH bond frequencies when the lone pairs were involved in complex formation.*

Rather better known is the post-war work which characterized CH_3O and CH_3N groups by their low-lying bands near 2800 cm^{-1}, which reflect the presence of weak CH bonds.[31]† Bohlmann first recognized that a lone pair weakens a CH

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*It is interesting to observe that these earlier conclusions have been recently vindicated by contemporary work in the overtone region, which has resulted in the 'local mode' description of CH stretching in CH_2 or CH_3 groups.[30]

†The suggestions in these papers that the 2800 cm^{-1} bands are due to 'symmetric' CH_3 stretching fundamentals are now seen to be erroneous. The more appropriate is the word 'fundamental', the less appropriate is the word 'symmetric'. This conclusion follows from quantitative descriptions based on the CHD_2 data.[35]

[29] R. Freymann and J. Gueron, *Compt. rend.*, 1937, **205**, 859; M. et R. Freymann, *Compt. rend.*, 1944, **219**, 515.

[30] B. R. Henry, *Accounts. Chem. Res.*, 1977, **10**, 207.

[31] H. B. Henbest, G. D. Meakins, B. Nicholls, and A. A. Wagland, *J. Chem. Soc.*, 1957, 1462; J. T. Braunholtz, E. A. V. Ebsworth, F. G. Mann, and N. Sheppard, *J. Chem. Soc.*, 1958, 2780; R. D. Hill and G. D. Meakins, *J. Chem. Soc.*, 1958, 760.

bond in the *trans* position, in studies of quinolizidine alkaloids.[32] Much work has since been done, both in n.m.r.[33] and in the i.r., in the latter notably by Krueger and co-workers.[34] However, $\nu(\mathrm{CH})^{\mathrm{is}}$ data were not obtained, so that a quantitative treatment of the bond strength was not possible.*

The first $\nu(\mathrm{CH})^{\mathrm{is}}$ values were reported by the author in the simplest CH_3N and CH_3O compounds in 1971.[4,35] Table 2 shows $\nu(\mathrm{CH})^{\mathrm{is}}$ data for these and some CH_3P and CH_3S compounds.[36,37] It is convenient to identify each CH bond by the group X lying *trans* to it, thus, $\nu(\mathrm{CH})^{\mathrm{X}}$. It is seen that $\nu(\mathrm{CH})^{\mathrm{lp}}$ is considerably lower than $\nu(\mathrm{CH})^{\mathrm{H}}$ or $\nu(\mathrm{CH})^{\mathrm{Me}}$ in the N and O compounds, its lowness increasing with the number of methyl groups, and decreasing with the number of lone pairs.† Where there are two of the latter, as in CH_3O species, there are *two* CH bonds *trans* to lone pairs, if these are visualized as in a Nyholm–Gillespie model, and accordingly two weak CH bonds are found. Extension of this idea to CH_3F leads us to expect three weak CH bonds here, and indeed the CH bond in this molecule is anomalously weak compared with CH_4 or CH_3Cl.[4] Although CH_3P and CH_3S compounds are also electron donors, the larger size of the P or S atom and their differing valence angles lead one to anticipate smaller *trans* effects. Such effects are indeed found to be small, zero, or even reversed,[37] as the data in Table 2 show.

Mechanism of the Lone Pair trans *Effect*. Insofar as *ab initio* calculations reproduce the bond strength variations very well, it may be said that the computer knows the physical cause of this effect, the difficulty lying in translating information concerning MO eigen-functions and values into intuitive pictures. Two prominent features of the population analyses are the higher charge densities found on the *trans* hydrogens, and much larger off-diagonal antibonding terms between these same hydrogens and the nitrogen, than for hydrogens *gauche* to the lone pair.

These results are in keeping with the n.m.r. evidence that the *trans* hydrogen is more screened than the *gauche* one and with the suggestion of Hamlow *et al.*[33] that the lone pair is partly delocalized into an antibonding σ orbital in the *trans* CH bond. In VB terms this would be equivalent to a repulsion between the CH bonding pair and the lone pair of electrons. A similar explanation, in terms of a Nyholm–Gillespie picture, has been given for the *tilt* of the methyl group, away

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**e.g.* derivatives such as $(CH_3)_2CDNH_2$ were studied and low $\nu(\mathrm{CD})$ bands found where CD was *trans* to the lone pair. CD stretching modes however are not good characteristic group frequencies, and in addition are often subject to Fermi resonances. See also ref. 42.

†We note an ambiguity in defining a lone pair *trans* effect. It could refer to the absolute weakness of $\nu(\mathrm{CH})^{\mathrm{lp}}$, or to the difference between $\nu(\mathrm{CH})^{\mathrm{lp}}$ and $\nu(\mathrm{CH})^{\mathrm{H}}$ and/or $\nu(\mathrm{CH})^{\mathrm{Me}}$. The distinction is clearly unimportant in CH_3N and CH_3O compounds.

[32] F. Bohlmann, *Chem. Ber.*, 1958, **91**, 2157.

[33] H. P. Hamlow, S. Okuda, and N. Nakagawa, *Tetrahedron Letters*, 1964, 2553.

[34] *e.g.* P. J. Krueger, J. Jan, and W. Wieser, *J. Mol. Structure*, 1970, **5**, 375; P. J. Krueger and J. Jan, *Canad. J. Chem.*, 1970, **48**, 3229, 3236.

[35] D. C. McKean and I. A. Ellis, *J. Mol. Structure*, 1975, **29**, 81.

[36] J. Travert, O. Saur, A. Janin, and J. C. Lavalley, *J. Mol. Structure*, 1976, **33**, 265.

[37] D. C. McKean and G. P. McQuillan, submitted for publication in *J. Mol. Structure*.

Table 2 $\nu(\mathrm{CH})^{\mathrm{is}}$ *and lone-pair* trans *effects*

	$\nu(\mathrm{CH})^{\mathrm{Me}}/\mathrm{cm}^{-1}$	$\nu(\mathrm{CH})^{\mathrm{H}}/\mathrm{cm}^{-1}$	$\nu(\mathrm{CH})^{\mathrm{lp}}/\mathrm{cm}^{-1}$	$\Delta r_0(pred.)^a/\text{Å}$	$\Delta r_e(ab.\,in.)^a/\text{Å}$	$\Delta D^\circ_{298}{}^b/$ kcal mol^{-1}
$CH_3NH_2{}^c$		2955	2880	0.008	0.009^d	6.5
$(CH_3)_2NH^c$	2962	2937	2834	0.013, 0.011	$0.010, 0.009^e$	11.0, 8.9
$(CH_3)_3N^c$	2952		2799	0.016	0.015^f	13.2
CH_3OH^g		2979	2920	0.006	0.006^h	5.1
$(CH_3)_2O^g$	2984		2884	0.010(5)	0.008^h	8.6
$CH_3PH_2{}^i$		2964	2979	−0.001(5)		1.3
$(CH_3)_2PH^i$	2962	2952	2949	0.001(5),0		1.1
$(CH_3)_3P^i$	2954		2919	0.003(5)		3.1
CH_3SH^j		2985	2982	~0		~0
$(CH_3)_2S^i$	2979		2947	0.003(5)		2.8

[a] $\Delta r - r_{\mathrm{CH}}{}^{\mathrm{lp}} - r_{\mathrm{CH}}{}^{\mathrm{Me/H}}$; [b] $\Delta D^\circ - D^\circ{}_{\mathrm{CH}}{}^{\mathrm{Me/H}} - D^\circ{}_{\mathrm{CH}}{}^{\mathrm{lp}}$; [c] ref. 35; [d] ref. 38; [e] ref. 39; [f] ref. 37; [g] ref. 4; [h] ref. 22*b*; [i] ref. 37; [j] ref. 36; $\nu(\mathrm{CH})^{\mathrm{is}}$ data for CH_3OPCl_2, CH_3COOCH_3 and $HCOOCH_3$ are quoted in ref 7, p. 1049.

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[38] P. Pulay and F. Torok, *J. Mol. Structure*, 1975, **29**, 239.

[39] (*a*) S. Skaarup, L. L. Griffin, and J. E. Boggs, *J. Amer. Chem. Soc.*, 1976, **98**, 3140; (*b*) E. Flood, P. Pulay, and J. E. Boggs, *J. Amer. Chem. Soc.*, 1977, **99**, 5570.

from the CN direction, in $(CH_3)_2NH$.[39] The author has suggested[35] that since a non-bonding repulsion is a mutual effect, the decrease in ionization potential of the lone pair in the series $MeNH_2$, Me_2NH, Me_3N may be due to the cumulative effect of repulsions from the *trans* CH bonds in each methyl group. However it is then difficult to see why the $\nu(CH)^{lp}$ value falls with increasing methyl substitution unless (i) there is a direct 'γ' repulsion effect between the methyl groups, as suggested by Bellamy and Mayo,[40]* or (ii) the character of the lone pair orbital is altered by replacement of the σ_{NH} bond by the σ_{NC} bond. The latter could then alone be responsible for the change in ionization potential. However it would seem prudent to include a 'back' *trans* effect as contributing to the changes in IP observed.

Wider Implications of the trans *Effect*. These have been well reviewed by Bellamy and Mayo.[41]† *trans* Effects of lone pairs should be, and can be found, affecting not only CH but NH and OH bonds. There seems no reason also why they should not likewise affect C—C or C—X bonds generally, and indications may be found that this is so.[41] If however C—C bonds are less affected than C—H, then the *trans* effect will have a significant role to play in determining the relative stabilities of the conformers of pyridine-type molecules. The effect will then tend to favour conformers in which the lone pair is *trans* to C—C (NH axial), contrary to the preferred conformation in which NH is equatorial.[42]

Lone pair *trans* effects should also occur across C=O and C=N bonds (see Section 3B) and various authors[29,41,43] have suggested that the well-known weakness of the aldehydic bond arises from this cause.

The lone pair *trans* effect is also a useful *tool* in conformational problems, *e.g.* the studies of dioxalane, dioxane, and other —CHRO— systems by Lavalley and co-workers;[44,45] also, of pyridines.[42] Another example, of different type, involves the disappearance of the effect when the lone pair is removed from the nitrogen *internally*, as for instance when CH_3 is replaced by SiH_3 or SiF_3.[35] The low i.r. band at 2865 cm^{-1} (gas), (2845 cm^{-1}, liquid) in $B[N(CHD_2)_2]_3$ suggests that the BNC_2 group is pyramidal, whereas the corresponding band at 2924 cm^{-1} (gas) in $Cl_2BN(CHD_2)_2$ is in keeping with a planar skeleton.[46]

B. HC=O and HC=N Systems.—For many CH=O systems, the observed $\nu(CH)$ values of the normal species, which are well known, are sufficiently low to be regarded as $\nu(CH)^{is}$, although Fermi resonances with $2\delta(CH)$ may remain. Table 3 lists the most reliable of these, to illustrate several notable features. Firstly, the α effect of methyl is a depression of about 43 cm^{-1}, as found in

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*See Section 3D. However the 4-31 G calculation for $(CH_3)_3N$ shows positive overlap between each of the H^{lp} atoms.[24]

†A possible application in the chlorination of ethers[20] was noted earlier (Section 3B).

[40] L. Bellamy and D. W. Mayo, to be published.

[41] L. J. Bellamy and D. W. Mayo, *J. Phys. Chem.*, 1976, **80**, 1217.

[42] I. D. Blackburne, A. R. Katritzky, and Y. Takeuchi, *Accounts. Chem. Res.*, 1975, **8**, 300.

[43] D. C. McKean, *Spectrochim. Acta*, 1975, **31A**, 1167.

[44] O. Saur, A. Janin, J. C. Lavalley, and N. Sheppard, *Compt. rend.*, 1973, **276**, *B*, 725.

[45] O. Saur, A. Janin, A. Vallet, and J. C. Lavalley, *J. Mol. Structure*, 1976, **34**, 171.

[46] Data from H. J. Becher, personal communication.

Table 3 $\nu(\mathrm{CH})^{\mathrm{is}}$ *in some* H—C=O *and* H—C=N *systems*

	$\nu(\mathrm{CH})^{\mathrm{is}}$		$\nu(\mathrm{CH})^{\mathrm{is}}$		$\nu(\mathrm{CH})^{\mathrm{is}}$
HCHO	2813^{a}	FCHO	2981^{b}	CHOCHO	2850^{b}
CH_3CHO	2770^{a}	HOCHO	2943^{a}	HSCHO *t, c*	2843, 2845^{c}
CH_3CHO,BF_3	2940^{b}	CH_3OCHO	2930^{a}	HC≡CCHO	2858^{a}
PhCHO	2770^{a}	CH_2=CHCHO	2800^{b}	CCl_3CHO	2856^{d}
$PhCHO,BF_3$	2930^{b}	NH_2CHO	2852^{a}	CBr_3CHO	2845^{d}
$HCOO^-$	$(2816)^{b}$				
CH_3CH=NCH_3	2839^{e}	CH_2=NH	3018^{f} 2936^{f}		

[a]ref. 7; [b]ref. 28*c*; [c]ref. 47; [d]ref. 48; [e]from the species CD_3CH=NCD_3;[24] see also ref. 50; [f]ref. 49. Whether these frequencies are truly $\nu(\mathrm{CH})^{\mathrm{is}}$, seems doubtful.

alkanes (see below). Secondly, certain substituents, *viz.* F, HO, CH_3O, produce very large increases in ν(CH), in the range of 120—170 cm^{-1}. Thirdly, complexing with BF_3 also produces large upward frequency shifts. A fourth observation of considerable interest is that $\nu(\mathrm{CH})^{\mathrm{is}}$ in HCOSH is almost identical in its *cis* and *trans* isomers, this apparently indicating the absence of any effect on ν(CH) of H–H interaction in this molecule.[47] The success of semi-empirical CNDO calculations has already been mentioned;[28] the physical reasons for the variations however remain obscure. *Ab initio* calculations on H_2CO and CH_3CHO show clearly an unusually high negative charge on the aldehyde hydrogen, and similarly high negative overlap populations between the latter and the oxygen. The weakening effect of the methyl group appears to arise from greater $H_{ald} \cdots O$ and $H_{ald} \cdots C_{Me}$ antibonding (the latter compared with $H_{ald} \cdots H_{ald}$ in H_2CO) in CH_3CHO, the overlap between H_{ald} and all three methyl hydrogens being positive.[24]

In CH=N systems, Bellamy and Mayo[41] found good evidence for low ν(CH) values associated with the expected lone pair *trans* effect in a number of cases, *e.g.* CH_2=NOH. However the only secure value of $\nu(\mathrm{CH})^{\mathrm{is}}$ known so far is that for MeCH=NMe (2839 cm^{-1}), which exists only in the conformer in which the CH bond is *trans* to the lone pair.

C. α Effects of Methyl, Halogens, CCl_3, and CF_3, in Saturated Compounds.— These are shown in Table 4. The α effect of methyl is always a depression of $\nu(\mathrm{CH})^{\mathrm{is}}$, by an amount varying from 42 to 19 cm^{-1}. It diminishes with an increase in the number of methyl groups, as seen in the series CH_4, $MeCH_3$, Me_2CH_2, and Me_3CH, and it is reduced by the successive addition of chlorine atoms.

The α effect of Cl has been most studied.[18,19] This is a rise in frequency which

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[47] W. H. Hocking and G. Winnewisser, *Z. Naturforsch.*, 1976, **31a**, 422, 438, 995.

[48] G. Lucazeau and A. Novak, *Spectrochim. Acta*, 1969, **25A**, 1615.

[49] C. B. Moore, G. C. Pimentel, and T. D. Goldfarb, *J. Chem. Phys.*, 1965, **43**, 63.

[50] H. Hollenstein and Hs. H. Günthard, *Chem. Phys.*, 1974, **4**, 368.

Table 4 *Some α-substitution effects on $\nu(\mathrm{CH})^{is}$ in saturated compounds*

	$\nu(\mathrm{CH})^{is}$	S_α^{F}		$\nu(\mathrm{CH})^{is}$	S_α^{F}		$\nu(\mathrm{CH})^{is}$	S_α^{F}
CH_4	2992		$\mathrm{Me}\mathit{CH}_3$	2950		$\mathrm{Me}_2\mathit{CH}_2$	2920	
CH_3F	2976	-16	$\mathrm{Me}\mathit{CH}_2\mathrm{F}$	2950	0	$\mathrm{Me}_2\mathit{CH}\mathrm{F}$	2931	11
CH_2F_2	2984	8						
CHF_3	2990^a	6^a						
		S_α^{Cl}			S_α^{Cl}			S_α^{Cl}
CH_3Cl	3012	20	$\mathrm{Me}\mathit{CH}_2\mathrm{Cl}$	2983	33	$\mathrm{Me}_2\mathit{CH}\mathrm{Cl}$	2962	42
CH_2Cl_2	3025	13	$\mathrm{Me}\mathit{CH}\mathrm{Cl}_2$	3006	23			
$CHCl_3$	3034	9						
		S_α^{Br}			S_α^{Br}			S_α^{Br}
CH_3Br	3027	35	$\mathrm{Me}\mathit{CH}_2\mathrm{Br}$	2996	46	$\mathrm{Me}_2\mathit{CH}\mathrm{Br}$	2975	55
CH_2Br_2	3040	13						
$CHBr_3$	3050	10						
		S_α^{I}			S_α^{I}			S_α^{I}
CH_3I	3029	37	$\mathrm{Me}\mathit{CH}_2\mathrm{I}$	2998	48	$\mathrm{Me}_2\mathit{CH}\mathrm{I}$	2974	54
CH_2I_2	3037	8						
CHI_3	3026	-11						
		$S_\alpha^{CF_3}$			$S_\alpha^{CCl_3}$			S_α^{CN}
$CH_3CF_3^b$	3010	18	CH_3CCl_3	2988	-4	CH_3CN	2985	-7
$CH_2(CF_3)_2^b$	3008	-2	CH_2ClCCl_3	3000	-12	$CH_2(CN)_2$	2963	-22
$CH(CF_3)_3^b$	2992	-16	$CHCl_2CCl_3$	3002	-23			

S_α^X values are the increments in $\nu(\mathrm{CH})^{is}$ due to successive α subsitution of X for H; S_α^{Me} can be obtained from horizontal differences in $\nu(\mathrm{CH})^{is}$. Data from refs. 7, 18, and 19 except where otherwise indicated.

[a] Considerable uncertainty due to Fermi resonance, ref. 51; [b] H. Bürger, personal communication.

is progressively smaller the more chlorines that are added. The α effect of Cl, however, is enhanced by methyl substitution. It seems as though the initial depression by α methyl makes possible a higher subsequent elevation by chlorine, in contrast to the effect noted above of the effect of chlorine on α methyl substitution. It is also in contrast to the effect of CCl_3 which greatly reduces the effect of α Cl.

The effects of α bromine and α iodine are elevations which initially are greater than those of chlorine, but which thereafter are similar, or as in the case of CHI_3, reversed. Fluorine behaves anomalously amongst the halogens in that the first fluorine gives a marked depression, attributed to a lone pair affect,[4] whereas the second and third give only small increases.*

The variations in these α effects on CH bonds are in contrast to the α effects found in SiH bonds. In the latter, S_α^{Me} is essentially constant, at about $-20\ cm^{-1}$, while S_α^{F} and S_α^{Cl} appear to increase marginally with successive addition of halogen, S_α^{F} being positive from the beginning.[18]

The α effect of a CX_3 group can also be considered as the β effects of the CX bonds concerned and it is in this context that models for the mechanism of the α effect have been discussed (see Section 3D).

D. β Effects of Methyl and Halogens, in Saturated Compounds.—A group placed in a β position may in general produce different effects depending on whether the CH bond affected is *trans* or *gauche* to the substituent. It is not easy to decide how best to describe the effects found. In some cases the simplest method is to quote $\nu(CH)^{is}$ values classified according to the group lying in the *trans* position, as in Table 5 which summarizes the data for all the ethyl, isopropyl, and t-butyl halides. Three main features are seen. The value for $\nu(CH)^{is}$ for a CH bond *trans* to halogen falls in the sequence F > Cl > Br > I, the extent of the fall increasing with the addition of methyl groups. The starting point of each series, however, differs, thus S_t^{F} takes the values +7 (EtF), +22 (i-PrF), +36 (t-BuF). Again, S_t^{Cl} starts negative (−5, EtCl) and then becomes positive (+5 in i-PrCl, +12 in t-BuCl). The second feature is the constancy of the $\nu(CH)^{is}$ values *trans* to CH_3 or H as the halogen is varied. Since these are all *gauche* to halogen, this could be described as a constant *gauche* effect of halogen, which is a consistent rise of 20—24 cm^{-1} compared with the corresponding hydrogen compound. The third feature is that the bonds *trans* to CH_3 are consistently 14—19 cm^{-1} stronger than those *trans* to H, *in the same molecule*. A larger difference (25 cm^{-1}) is found in CH_3NHMe. This could be termed a *gauche* effect of methyl, providing it is realised that this difference is in fact $S_t^{Me} - S_g^{Me}$ in terms of the definition of S. The value of $S_t^{Me} - S_g^{Me}$ is more constant than is that of S_t^{Me} alone. Thus S_t^{Me} from a comparison of propane with ethane is 0, but from the pair Me_2CH_2/Me_3CH it is +7 cm^{-1}, and from Me_4C/Me_3CH, +10 cm^{-1}. S_g^{Me} is more constant: −14 cm^{-1} from the pair CH_3CH_2Me/CH_3CH_3, −12 cm^{-1} from CH_3CHMe_2/CH_3CH_2Me and −13 cm^{-1} from CH_3NHMe/CH_3NH_2.

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*The value of $\nu(CH)^{is}$ for CHF_3 is uncertain due to a strong Fermi resonance.[51]

[51] C. C. Costain, *J. Mol. Spectroscopy*, 1962, **9**, 317.

Table 5 *β-substitution effects of* Me *and halogen on* ν(CH)$^{\mathrm{is}}$ *in saturated compounds*[a]

	groups lying trans		
	CH$_3$	H	X
CH$_3$CH$_2$—H		2950	
F		2973	2957
Cl		2972	2945
Br		2971	2936
I		2969	2928
CH$_3$MeCH—H	2950	2936	
F	2974	2958	2958
Cl	2976	2959	2941
Br	2976	2958	2929
I	2973	2955	2918
CH$_3$Me$_2$C—H	2943	2924	
F	2967		2960
Cl	2968		2936
Br	2971		2925
I	2968		2909
CH$_3$CHCl$_2$		2984	2971
CH$_3$CCl$_3$			2988
CH$_3$CMeCl$_2$	2993		2966

[a] The ν(CH)$^{\mathrm{is}}$ values listed are for CH bonds in the methyl group *in italics*, data from ref. 18 and 19; β effects of methyl in CH$_3$—N, P, O, and S compounds can be seen in Table 2.

The reliability of the value of $S_t^{\mathrm{Me}} - S_g^{\mathrm{Me}}$ leads to the prediction that in cyclohexanes, the equatorial CH bond will be stronger than the axial one, by 2—5 kcal mol^{-1}, since the former is *trans* to two C—C bonds, the latter *trans* to two CH ones.*

A tabulation of S_g and S_t effects for both methyl and chlorine for chloroalkanes is included in ref. 18, mainly to draw attention to the high degree of non-additivity they exhibit. A general conclusion for S^{Cl} values is that both S_α^{Cl} and S_β^{Cl} effects diminish with increasing numbers of chlorine atoms.

It is plain that the *trans* and *gauche* effects of halogen cannot be easily related to the normal pattern of inductive effects.

Chemical models for β-substitution effects. Two models have been suggested, both based on the premise of repulsions between the terminal atoms, or bonding pairs of electrons involved, in the β bonds. The Reporter, starting from the above VB description of the lone pair *trans* effect, has speculated that such repulsions also occur between two bonding pairs of electrons, similarly related. In this way, the decreasing strength of the CH bond with α methyl substitution in the series CH$_4$, CH$_3$Me, CH$_2$Me$_2$, CHMe$_3$ is attributed to the increasing number of repulsions involving the *trans* CH bonds in each methyl group.[12] The varying *trans* effect of

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*This has now been confirmed[55] (J. Caillod, O. Saur and J. C. Lavalley, to be published). The difference in strength is 31 cm^{-1} ≡ 2.7 kcal mol^{-1}; see also ref. 45.

halogen in the alkyl halides is then attributed to a progressive 'loss of control' by the halogen of the CX bonding electrons, in the order F > Cl > Br > I, with a resultant increase in the repulsion between this pair and the pair in the *trans* CH bond.[43]*

Bellamy and Mayo,[40] by contrast, suppose *gauche* H · · · H (or bonding pair) repulsions to dominate both CH bond strength, and also CH_3 HCH angles, *gauche* H · · · X repulsions being held to be insignificant. The fall in $\nu(CH)^{is}$ of 42 cm^{-1} from CH_4 to CH_3Me is then due to the *gauche* effect of two hydrogens. This then leads to an explanation of the constant *gauche* effect of halogen of about $+20$ cm^{-1}, since a CH bond *gauche* to halogen in CH_3CH_2X is now *gauche* to only one CH bond, and the repulsion from the *gauche* CX is considered insignificant in all cases. The $\nu(CH)^{is}$ consequently rises one half of the way back to the value in CH_4. If two or three β halogens are present, the CH bond may be *gauche* only to two halogens and a $\nu(CH)^{is}$ value close to that in CH_4 is then expected, and indeed found.

The varying *trans* effect of halogen is attributed in this work[40] to changes in HCX angles, with changes of halogen. Bellamy and Mayo extend their invocation of repulsions between hydrogen atoms to explain the *gauche* effect (or rather, $(S_t^{Me} - S_g^{Me})$ of methyl described above. Here the repulsions invoked involve CH bonds γ to each other. Slight support for part of the Bellamy–Mayo model comes from studies of β CH—CH stretch–stretch interaction force constants.[26] The constant involving *gauche* bonds is positive, as expected for a repulsion between the hydrogens. By contrast, the constant for *trans* bonds is negative, in agreement with population analyses from *ab initio* calculations[24] which show positive (bonding) terms between *trans* hydrogens, but negative (antibonding) ones between *gauche* ones. These overlap populations are of course connected with the *ab initio* force constants, which for ethane have the same signs and fairly similar magnitudes to those found by experiment.[26b] However, the overlap populations for γ hydrogens in close proximity, are positive,[24] as noted also by Cremer *et al.*[52] in connection with barriers to restricted rotation, so that no support is given to the Bellamy–Mayo explanation of the *gauche* effect of methyl.

A further consideration is that these β or γ overlap populations are all smaller by a power of ten than the α ones, acting between the H and X atoms in the system H—C—X, which are always negative. Moreover the correlation between CH bond strengths and HCH angle works equally well for CH_3X compounds in which X is halogen, CN, $C{\equiv}CH$, NO_2, BF_2, BCl_2, Ph, as it does for CH_3Me.[14] These represent a wide range of $\nu(CH)^{is}$ values in situations where no β CH bonds are present. The implications seem to be that it is the nature of the X group and the CX bond which determine the HCH angle and perhaps also the CH bond strength.

Exploration of the substitution effects of halogen by *ab initio* calculations is

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*Supposing the carbon 2*p* character to be responsible for the repulsion,[39b] this may be expected to increase in the series F, Cl, Br, or I.

[52] D. Cremer, J. S. Binkley, J. A. Pople, and W. J. Hehre, *J. Amer. Chem. Soc.*, 1974, **96**, 6900.

restricted to fluorine and chlorine compounds.[24] The results have been disappointing. The 4–31G basis set describes very poorly both the α effect of F or Cl, and the combined α effects of halogen and methyl. The β effects of halogen are somewhat better reproduced, the constant *gauche* effect exactly so. The difference in r_e for CH^{X} between fluorine and chlorine is somewhat greater [0.003(4) Å] than the $\nu(\text{CH})^{\text{is}}$ data imply (0.001(2) Å).

E. Substitution Effects on Olefinic CH Bonds.—$\nu(\text{CH})^{\text{is}}$ data are available for the effects of methyl groups[1] and halogen atoms[43] on CH bonds in positions *cis*, *trans*, and α to the substituent, although the data are less accurate than those for saturated compounds since partial deuteriation does not in general remove resonances in the CH stretching region arising from $\nu(\text{C}{=}\text{C})$ and $\delta({=}\text{CH})$ levels. The reference compound, ethene, has a current $\nu(\text{CH})^{\text{is}}$ value of 3055 cm^{-1}.[23]

Table 6 *Substituent effects on olefinic* CH *bonds*[a,b]

	$\nu(\text{CH})^{\text{is}}$					
	H_c	H_t	H_α	S_c^{X}	S_t^{X}	S_α^{X}
$CH_2{=}CHMe$[c]	3039	3064	3013	−16	9	−42
CH_2 $CHCl$[d]	3074	3072	3082	19	17	27
CH_2 $CHBr$[d]	3074	3057	3085	19	2	30

[a] reference compound C_2H_4, 3055 cm^{-1};[23] [b] for other halogenated ethylenes, see ref. 43; [c] ref. 1; [d] ref. 43.

Table 6 shows experimental $\nu(\text{CH})^{\text{is}}$ values for propene, vinyl chloride, and bromide, and the S values obtained from them. S_α for methyl is $-42\ \text{cm}^{-1}$, identical with its value in ethane.* The *trans* and *cis* effects of methyl are positive and negative, respectively, rather like the *trans* and *gauche* ones in saturated compounds. It is interesting to note that they predict, rather well, the observed frequency of 3050 cm^{-1} in but-1-ene [$S_c^{\text{Me}} + S_t^{\text{Me}} = -7$, $\nu(\text{CH})^{\text{is}}$ (pred.) = 3048 cm^{-1}].

The α and *cis* effects of chlorine and bromine are also like the α and *gauche* effects in saturated compounds. The *trans* effects are however both positive. in contrast to the alkyl halides, although, as in the latter, $S_t^{\text{Cl}} > S_t^{\text{Br}}$.

Since no $\nu(\text{CH})^{\text{is}}$ data are available as yet for vinyl fluoride and iodide, the CH stretching frequencies of di- and tri-halogenated ethylenes have been examined for indirect evidence of substituent effects.[43] It seems very probable that the sequence $S_t^{\text{F}} > S_t^{\text{Cl}} > S_t^{\text{Br}} > S_t^{\text{I}}$ is even more marked in ethylenes than it is in alkyl halides; also that fluorine markedly strengthens CH bonds in the α, *cis*, and *trans* positions.. The *cis* effect in an ethylene would of course be expected to resemble an *ortho* effect in an aromatic compound. Bellamy and Mayo[40] quote $\nu(\text{CH})$ data for benzenes which suggest a strong similarity with the ethylenes: *e.g.* for 1:3:5 benzene-X_3, X = D, 3053 cm^{-1}; F, 3108; Cl, 3089; Br, 3090; Me, 3020

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*With reference to the Bellamy–Mayo model for S_α^{Me}, the *gauche* H—H distance in propene is 0.035 Å greater than that in ethane.

cm^{-1}. In these compounds the ν(CH) modes are essentially isolated; however, each CH bond is subject to one *para* and two *ortho* effects of X. The similarity to S_{cis} effects therefore suggests that S_{para} is either negligible, or similar to S_{ortho}.

The success of *ab initio* calculations of r_e in predicting the effect of methyl on =CH in propene can be seen in Table 1. However these calculations exhibit one curious feature; if the remaining geometrical parameters are constrained to their spectroscopic values, no differences in r_e(CH) emerge. Only when the C=C bond in particular is allowed to refine to an optimum 0.02 Å less than the r_s value, do the expected differences appear.

Preliminary calculations on the vinyl halides do not merit space here.

F. Methyl Groups Adjacent to Multiple Bonds: Hyperconjugation.—The data available so far are shown in Table 7, where H_s and H_a refer to atoms in and out of the skeletal plane respectively. In these four C=X compounds, CH_a is always weaker than CH_s. This might be attributable to hyperconjugation, since the latter, as normally conceived, involves a movement of charge out of an MO involving the H_a hydrogen into the rest of the molecule. Mulliken[53] has estimated that this should weaken the CH_a bonds by about 0.001 Å, corresponding to about 10 cm^{-1} in $\nu(CH_a)^{is}$. The H_s—H_a difference, however, is considerably more than this, especially in the C=O compounds. *Ab initio* calculations suggest that part of this may arise in a different manner. On the one hand, the net atomic population on H_a in propene is appreciably greater than that on H_s[24] although the gross populations are similar. On the other, the dipole moment in propene is said to arise largely from a polarization of the π bond away from the methyl group.[54] Together these findings suggest that the main effect in propene is a non-bonding electron pair repulsion between the π electrons and the CH_a bonding pairs. In acetaldehyde, both the net and gross populations are larger on H_a than on H_s, although hyperconjugation would have been expected to be greater than in propene. The tentative conclusion is that hyperconjugation, if it exists, is masked by other, stronger, influences. Loss of charge from the CH_s atom seems to be correlated with a *rise* in CH bond strength.

Where a methyl group is attached to a triple bond, all these CH bonds will be involved in either loss of charge, due to hyperconjugation, or in repulsion involving the π bonds. It is therefore interesting to observe that the CH bond is markedly stronger in CH_3CN than it is in $CH_3C{\equiv}CH$. The 4–31G basis set can reproduce the difference in bond length (Table 8) but only provided all the bonds are allowed to vary in length. Both net and gross populations on the hydrogens are larger in the acetylene. As would be expected intuitively, the CH bond is slightly weaker in CH_3—C≡C—CH_3 than in CH_3—C≡CH.

Returning briefly to the C=X compounds, we note that the β effects of the second methyl group on the *trans* and *gauche* CH bonds of the first one, are

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[53] R. S. Mulliken, C. A. Rieke, and W. G. Brown, *J. Amer. Chem. Soc.*, 1941, **63**, 41.

[54] L. Radom, W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Amer. Chem. Soc.*, 1971, **93**, 5339.

Table 7 *$\nu(CH)^{is}$ values for methyl groups adjacent to multiple bonds*

	$\nu(CH)^{is}$/cm^{-1}	r_0(*pred.*)/Å	r_e(4—31G)/Å	*n.a.p.*^{a}/e	*g.a.p.*^{a}/e	D°_{298}(*pred.*)/ kcal mol^{-1}
A. double bonds						
CH$_3$CH CH$_2$						
H$_s$	2959^{b}	1.095(5)	1.082^{c}	0.540	0.838	100.4
H$_a$	2931^{b}	1.098(5)	1.085^{c}	0.555	0.836	98.0
H$_s$ − H$_a$	28	−0.003	−0.003	−0.015	+0.002	2.4
(CH$_3$)$_2$C=CH$_2$						
H$_s$	2965^{b}	1.095				100.9
H$_a$	2924^{b}	1.099				97.4
H$_s$ − H$_a$	41	−0.004				3.5
CH$_3$CHO						
H$_s$	3002^{b}	1.091	[1.079(5)]^{a,d}	[0.491]^{d}	[0.794]^{d}	104.1
H$_a$	2945^{a}	1.097	[1.085(5)]^{a,d}	[0.518]^{d}	[0.813]^{d}	99.2
H$_s$ − H$_a$	57	−0.006	−0.006	−0.027	−0.109	4.9
(CH$_3$)$_2$CO						
H$_s$	3004^{a}	1.091				104.3
H$_a$	2946^{b}	1.097				99.3
H$_s$ − H$_a$	58	−0.006				5.0
B. triple bonds						
CH$_3$C≡CH	2958^{e}	1.095(5)	1.082(8), [1.082(3)]^{a,d}	0.515	0.807	100.3
CH$_3$C≡CCH$_3$	2950^{f}	1.096(5)				99.6
CH$_3$C—N	2985^{g}	1.093	1.080(5), [1.082]^{a,d}	0.476	0.780	102.6
CH$_3$N≡C	2989^{h}	1.092(5)	[1.081(3)]^{a,d}	[0.498]^{d}	[0.795]^{d}	103.0

[a]ref. 24; n/g.a.p. = net/gross atomic population; [b]ref. 1; [c]ref. 21; [d]unbracketed values: optimization of all bond lengths, bracketed values: optimization only of r_{CH}; [e]ref. 7; [f]ref. 55; [g]ref. 9; [h]ref 56.

[55] J. C. Lavalley, personal communication.

[56] D. C. McKean, J. L. Duncan, and M. Mackenzie, *J. Mol. Structure*, 1977, **42**, 77.

Table 8 $\nu(\text{CH})^{\text{is}}$ *and* CH *bond strength variations in* CH_3*-planar* XY_2 *compounds*[a]

	$\nu_{\parallel}{}^{b}/\text{cm}^{-1}$	$\nu_{\perp}{}^{b}/\text{cm}^{-1}$	$\Delta\nu^{c}/\text{cm}^{-1}$	$\Delta r_{o}{}^{c}/\text{Å}$	$\Delta r_{e}{}^{c}/\text{Å}$	$\Delta D^{\circ}_{298}{}^{c}/$ kcal mol^{-1}
CH_3NO_2	3065	3006	59	−0.006	−0.005	5.1
CH_3BF_2	2997	2937	60	−0.006	−0.006	5.2
$(CH_3BO)_3$	2987	2927	60	−0.006	−0.006(4)	5.2
CH_3BCl_2	2989	2916	73	−0.007(5)		6.3
$(CH_3)_3B$	2980	2884	95	−0.010	−0.007	8.2

[a] data from ref. 57, 58; [b] $\nu_{\parallel}$, $\nu_{\perp}$ signify $\nu(\text{CH})^{\text{is}}$ with hydrogen respectively in skeletal plane, and at right angles to it; [c] $\Delta\nu = \nu_{\parallel} - \nu_{\perp}, \Delta r = r_{\parallel} - r_{\perp}$ *etc.*

normal for but-1-ene, ($S_t^{Me} = +6$, $S_g^{Me} = -7$ cm^{-1}) but that in acetone they are both zero within the experimental error.

G. Methyl Groups Attached to Planar XY_2 Skeletons.—A methyl group so attached experiences a very low potential barrier to its internal rotation, and the latter is essentially free at ordinary temperatures. The vibrational spectra of such molecules present unusual features, not all of which are understood, but the studies of CHD_2 substituted $MeNO_2$,[57] $MeBF_2$, $MeBCl_2$, $(MeBO)_3$, and Me_3B[58] have left no doubt that the strength of the CH bond varies during the internal rotation, such that it is a maximum when in the plane of the skeleton, and a minimum when at right angles to it, with a total variation of $\nu(CH)^{is}$ between 60 and 95 cm^{-1}, as shown in Table 8. While no CHD_2 data in the gas phase are yet available for toluene, the existing spectra[59] give a sure indication of a similar alteration in strength with torsional angle. Here again, as in CH_3—C=X compounds, hyperconjugation may be invoked to explain the weakness of $CH_\perp$ (out-of-plane), and it is certainly true that the difference $\nu(CH)_\parallel - \nu(CH)_\perp$ is greatest in BMe_3, where the boron $2p_\pi$ orbital is essentially empty.

The population analyses from the *ab initio* studies of Mallinson[60] on $MeNO_2$, $MeBF_2$, and Me_3B are illuminating. In all these cases, $H_\parallel$ has a gross population 0.008—0.009 e greater than that of $H_\perp$. The π orbitals of the NO_2, BF_2, and B groups have gained from each methyl group, respectively, 0.021, 0.032, and 0.032 e. These, however, must be contrasted with gains in the σ orbitals of 0.45 e for the NO_2, 0.43 e for BF_2, and a loss of 0.033 (per Me) for the boron in Me_3B. Clearly the π effect can be insignificant compared with the σ one. Moreover, the CH overlap population is *higher* for $H_\perp$ than it is for $H_\parallel$ in $MeNO_2$ and $MeBF_2$, so that some other reason for $\nu(CH)_\parallel > \nu(CH)_\perp$ must be found. One factor in $MeNO_2$ may be the marked positive overlap between $H_\parallel$ and the *cis* oxygen. This is almost completely absent in $MeBF_2$, although the *cis* and *trans* effects of fluorine found in ethylenes (see Section 3E) should be present, affecting $H_\parallel$ here. However, for Me_3B, the CH overlap is slightly lower for $H_\perp$ than it is for $H_\parallel$, so that it remains possible to postulate hyperconjugation as a factor contributing here to the largest $\nu_\parallel - \nu_\perp$ difference found.

4 Conclusion

'Isolated' CH stretching frequencies constitute a unique source of quantitative information on the strengths of individual CH bonds. The present survey, limited as it is,* reveals patterns of conformational and substitutional effects which present new problems of chemical interpretation, although in part they are

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*The vast fields of aromatic and organometallic compounds are only represented by a single paper in each case.[61,62]

[57] D. C. McKean and R. A. Watt, *J. Mol. Spectroscopy*, 1976, **61**, 184.

[58] D. C. McKean, H. J. Becher, and F. Bramsiepe, *Spectrochim. Acta*, 1977, **33A**, 951.

[59] A. B. Dempster, D. B. Powell, and N. Sheppard, *Spectrochim. Acta*, 1975, **31A**, 245.

[60] P. D. Mallinson, personal communication.

[61] E. D. Schmid and F. Langenbucher, *Spectrochim. Acta*, 1966, **22**, 1621; see also ref 40.

[62] H. Bürger and S. Biedermann, *Spectrochim. Acta*, 1972, **28A**, 2283.

successfully predicted by quantum-mechanical methods. The new data have considerable implications also in the fields of chemical kinetics and of molecular geometry.

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