

Partial and absolute CH stretching frequencies and bond length differences have become measured quantities with direct link to each other via a single doublet bond length and overall orientation angle  $\langle \text{HCH} \rangle$ , determined from very strong  $\nu_{\text{CH}}$  bands and also from quite telling sets of three interconverting bond angles  $\langle \text{HCH} \rangle$  corresponding directly to which type of methyl group is present. These methods have been developed by using  $\nu_{\text{CH}}$  and  $\langle \text{HCH} \rangle$  to study the effect of partial deuteration on the spectra of  $\text{H}_2\text{O}$ ,  $\text{Bn}_2\text{O}$ ,  $\text{HO}-\text{Bn}_2\text{O}$  and related compounds.

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Author's Review

## Interpreting the CH Stretching Region, Through Infrared Partial Deuteration Studies

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Information derived from a study of 'isolated' CH stretching frequencies, measured in partially deuterated organic and organometallic compounds, is reviewed. This includes CH bond lengths and dissociation energies, and HCH angles in methyl groups. Excellent agreement is found between CH bond length differences predicted from  $\nu_{\text{CH}}^{1s}$  values and those calculated by *ab initio* methods.  $\nu_{\text{CH}}^{1s}$  data also agree with the results of high overtone, local mode studies in distinguishing differences in CH bond strengths. The former however are based on spectra which are easier to assign to specific bonds. They also enable one to understand the spectra of normal, undeuterated molecules in the CH stretching region, through 'energy factored force field' calculations.

Reference is made to situations involving free internal rotation of methyl groups, and to studies of other 'isolated' MH bonds ( $M = N, Si, Ge, Sn$ ).

### INTRODUCTION: 'ISOLATED' CH STRETCHING FREQUENCIES

The purpose of this article is to explain how the study of the vibrational spectra of partially deuterated compounds has revolutionised our understanding of the CH stretching region of the spectra of organic molecules, thereby yielding some fascinating insights into variations of CH bond strength which were previously unsuspected or unmeasurable.

A second objective will be to relate this type of study to two quite different approaches to the study of CH bonds, firstly, investigations of high overtone 'local mode' spectra of undeuterated species, and secondly, the *ab initio* quantum-mechanical calculation of molecular geometry.

The chemist has of course long been aware of the broad distinction in strength between acetylenic, olefinic and saturated hydrocarbon CH bonds, especially through the classic early work of Fox and Martin<sup>1</sup> on the characteristic CH stretching frequencies of these types of compound. If however one examines the vibrational spectrum, especially the infrared one, of any organic compound other than an acetylene or  $\text{CHX}_3$  one, it is almost always found to possess a complexity, which renders assignment of the bands hard enough, and the extraction of information about individual CH bond strength even harder.<sup>2</sup>

For this complexity there are three causes. The first is the obvious one that many types of CH bond may be present in any one compound. The

second and third causes are seen clearly in the case of a molecule like  $\text{CH}_3\text{Cl}$ , Figure 1, in which there is only one type of CH bond. The coupling between the three CH bonds gives rise to symmetric ( $\nu_s \text{CH}_3$ ) and antisymmetric ( $\nu_{as} \text{CH}_3$ ) vibrations and fundamental bands in the methyl group as a whole, displaced from each other by about  $100 \text{ cm}^{-1}$ , while a Fermi resonance between the upper vibrational level of the  $\nu_s$  band and the  $v_5 = 2$  upper state of the antisymmetric deformation mode  $\delta_{as} \text{CH}_3$  both imparts intensity to the  $2\delta_{as} \text{CH}_3$  band and displaces the  $2\delta_{as} \text{CH}_3$  and  $\nu_s \text{CH}_3$  bands away from each other.

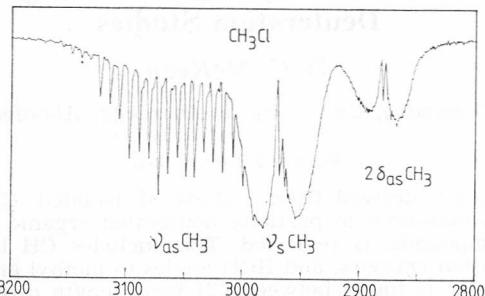


Figure 1. Infrared spectrum of  $\text{CH}_3\text{Cl}$  vapour, showing 3 bands, due to  $\nu_{as} \text{CH}_3$ ,  $\nu_s \text{CH}_3$  and  $2\delta_{as} \text{CH}_3$  respectively, the latter two in Fermi resonance with each other.

Extracting accurate information on the individual bond CH stretching force constant in these circumstances is then hard, if not impossible.

If however the simple expedient is adopted, of substituting two of the three hydrogens by deuterium, and of studying the spectrum of  $\text{CHD}_2\text{Cl}$ , Figure 2, just one  $\nu \text{CH}$  band is seen in the  $3000 \text{ cm}^{-1}$  region, whose frequency is a good measure of the strength of a single, isolated CH bond, since firstly the CD stretching vibrations occur much lower in frequency and are effectively decoupled from the  $\nu \text{CH}$  one, and secondly, the  $\delta \text{CH}$  modes occur near  $1300 \text{ cm}^{-1}$  and their overtones are not significantly in resonance with  $\nu \text{CH}$ .

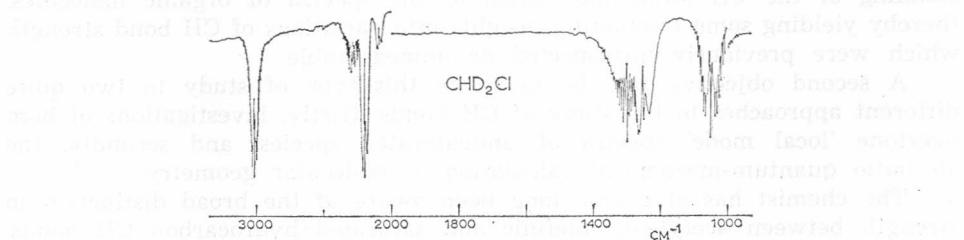


Figure 2. Infrared spectrum of  $\text{CHD}_2\text{Cl}$  vapour, showing a solitary  $\nu \text{CH}$  band at  $3012 \text{ cm}^{-1}$ , two  $\nu \text{CD}$  band near  $2200 \text{ cm}^{-1}$  and  $\delta \text{CH}$  bands near  $1300 \text{ cm}^{-1}$ .<sup>5</sup> (Reprinted by permission from *J. Mol. Struct.*<sup>16</sup>.)

Such frequencies, observed in partially deuterated compounds, and termed 'isolated' ones,  $\nu_{\text{CH}}^{\text{is}}$ , have been observed in passing for many years, but more especially since 1971, when their full significance was first realised.<sup>3</sup> A major review of the work in the 70's appeared in 1978,<sup>4</sup> and a minor one mainly relating to GeH and SiH bonds in 1984.<sup>5</sup>

One of the most pleasing results of the partial deuteration experiment is the appearance of several bands in the  $\nu_{\text{CH}}$  spectrum of a molecule in which conventional wisdom would have supposed only one type of CH bond to be present. Figure 3 illustrates the case of  $\text{CHD}_2$  substituted methylamines in which the mono and trimethyl compounds each exhibit two  $\nu_{\text{CH}}$  bands, the dimethyl compound, three. Each methyl group in fact contains either two or three CH bonds of different strength. The bonds concerned can be identified through the infrared gas phase band contours, which reveal the direction of the change of dipole moment during the vibration and hence the direction of the bond concerned.

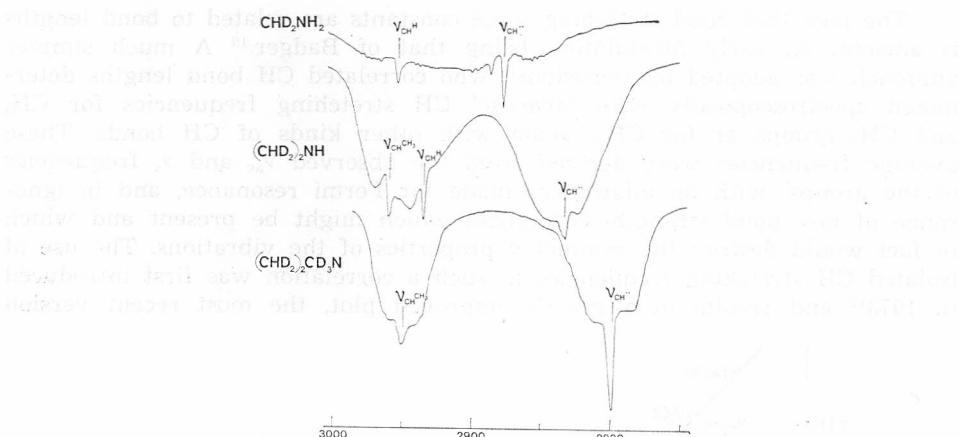


Figure 3. Infrared spectra of  $\text{CHD}_2$  labelled methylamines, showing the presence of different types of CH bond, the weakest in each case due to the bond *trans* (anti periplanar) to the lone pair of electrons ( $\text{CH}''$ ). The rotational contours help to identify the bonds concerned.<sup>5</sup> (Reprinted by permission from *J. Mol. Struct.*<sup>16</sup>)

The striking feature of Figure 3 is the presence of a single, abnormally weak bond in each molecule, whose weakness increases dramatically with the number of methyl groups. The bond concerned is the one which is '*trans*' or '*anti periplanar*' to the lone pair of electrons.<sup>6</sup> The existence of an effect peculiar to this bond has long been known<sup>7</sup> and is linked with other effects such as the '*anomeric*' one.<sup>8</sup> The point here is that the partial deuteration experiment yields a quantitative measurement of its extent, which is impossible in the undeuterated species. The latter are well known to possess low frequency '*Bohlmann*' bands near  $2800 \text{ cm}^{-1}$ , but these arise from varying mixtures of the motions of the different kinds of CH bonds on which is superimposed varying amounts of Fermi resonance.<sup>9</sup>

To return to the  $\text{CHD}_2$  spectra, however, the reader who is an NMR spectroscopist may well be surprised at the appearance of 2 or 3 bands from one and the same  $\text{CHD}_2$  group. In an NMR spectrum, if the three protons were non-identical, only an average proton resonance would be recorded, at room temperature at least, due to the rapid movement of the protons through or over the low potential barrier opposing internal rotation. However the time scale of the infrared experiment is so much shorter (the torsional splittings of the CH stretching vibrational levels are insignificant)

that the CH bonds are seen effectively as 'locked in' to one of the three potential minima, and so two or three bands can be observed.

The case of trimethylamine is of peculiar interest in that it exhibits the highest CH bond strength difference,  $150 \text{ cm}^{-1}$ , in a single methyl group yet encountered. It is indeed comparable with the difference between a saturated CH bond and an olefinic one, or an aldehydic one. This immediately prompts the thought, is such a difference in frequency reflected in a difference of bond length or of dissociation energy? This, we now consider.

#### CORRELATION BETWEEN $\nu_{\text{CH}}^{\text{is}}$ AND $r_0 \text{CH}$

The idea that bond stretching force constants are related to bond lengths is ancient, an early formulation being that of Badger.<sup>10</sup> A much simpler approach was adopted by Bernstein<sup>11</sup> who correlated CH bond lengths determined spectroscopically with 'average' CH stretching frequencies for  $\text{CH}_3$  and  $\text{CH}_2$  groups or for  $\text{CH}_4$ , along with other kinds of CH bonds. These average frequencies were derived from the observed  $\nu_{\text{as}}$  and  $\nu_s$  frequencies of the groups, with no allowances made for Fermi resonance, and in ignorance of any bond strength differences which might be present and which in fact would destroy the symmetry properties of the vibrations. The use of isolated CH stretching frequencies in such a correlation was first introduced in 1973<sup>12</sup> and results in a greatly improved plot, the most recent version

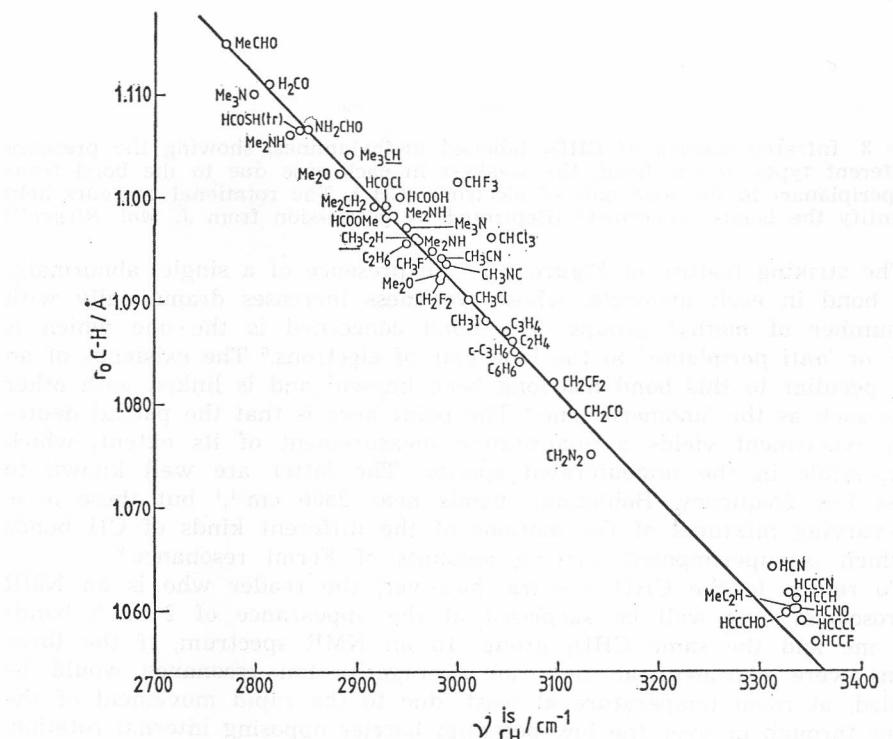


Figure 4. Correlation graph of  $r_0 \text{CH}$  determined from spectroscopic rotational constants versus  $\nu_{\text{CH}}^{\text{is}}$ . (Reprinted by permission from *J. Mol. Structure*<sup>5</sup>).

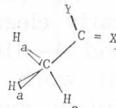
of which is shown in Figure 4.<sup>5</sup> It has first to be said that the positions of hydrogen atoms in molecules are notoriously difficult to pinpoint by experimental means. Due to the presence of zero point energy of vibration, each type of experiment — spectroscopic, electron or X-ray diffraction, yields a different kind of average CH bond length. One has to choose one particular method — in our case, the spectroscopic one, and stick to it. Within the spectroscopic approach, there are various methods of extracting geometry from the rotational constants which form the raw data. The present correlation uses data only for ' $r_o$ ' structures, for those cases where the CH bond lengths appear to be well determined.<sup>13</sup> Two molecules are of special interest here,  $\text{Me}_3\text{N}$  and  $\text{Me}_2\text{O}$ . In both of these the microwave based  $r_o$  structures indicate two different CH distances within each methyl group. In each case also there are two  $\nu_{\text{CH}}^{\text{is}}$  values, and the two pairs of points then lie very close to the overall correlation curve. The  $150 \text{ cm}^{-1}$  difference in  $\nu_{\text{CH}}^{\text{is}}$  in  $\text{Me}_3\text{N}$  indicates then an  $r_o$  CH difference of  $0.015 \text{ \AA}$  — a change whose significance can be brought out as follows. A change in  $\nu_{\text{CH}}^{\text{is}}$  of  $10 \text{ cm}^{-1}$  corresponds to a  $\Delta r_o$  CH value of  $0.001 \text{ \AA}$ . The effects of coupling etc. on  $\nu_{\text{CH}}^{\text{is}}$  in similar molecules probably introduces an uncertainty of the order of  $5 \text{ cm}^{-1}$ . Thus bond length differences in similar molecules should be predictable to  $\pm 0.0005 \text{ \AA}$ , which is far more accurate than any current direct experimental method.

#### COMPARISONS BETWEEN $\nu_{\text{CH}}^{\text{is}}$ PREDICTIONS AND *ab initio* CALCULATIONS

Quantum mechanical calculations of the *ab initio* variety can now readily be carried out both of the geometry and of the force fields of small to medium sized molecules. Because most people find force constants uninteresting and bond lengths more 'real', nearly all the interaction between  $\nu_{\text{CH}}^{\text{is}}$  studies and *ab initio* ones has been through the medium of the bond length changes which each method predicts. Of course, since the *ab initio* approach calculates 'equilibrium' geometries,  $r_e$ , such  $r_e$  CH bond lengths are not directly comparable with  $r_o$  CH ones predicted from  $\nu_{\text{CH}}^{\text{is}}$ .<sup>4</sup> Nevertheless the changes from one bond to another in  $\Delta r_e$  and  $\Delta r_o$  should run parallel, and this is indeed found.<sup>16,17</sup> Tables I and II compare  $\Delta r_e$  (*ab initio*) and

TABLE I

#### *CH Bond Length Differences Within Methyl Groups Attached to Double Bonds*



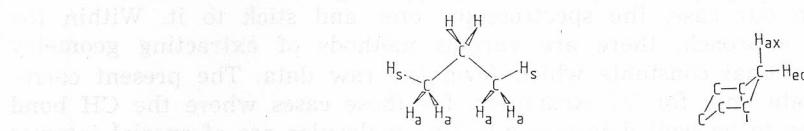
	$\Delta r_{\text{CH}} (\text{a} - \text{s})/\text{\AA}$ $\nu_{\text{CH}}^{\text{is}} \text{ ab. in.}^b$		$\Delta r_{\text{CH}} (\text{a} - \text{s})/\text{\AA}$ $\nu_{\text{CH}}^{\text{is}} \text{ ab. in.}^b$	
$\text{CH}_3\text{CHO}$	0.005 <sub>9</sub>	0.005 <sub>4</sub>	$\text{CH}_3\text{CH}=\text{CH}_2$	0.002 <sub>9</sub>
$\text{CH}_3\text{COMe}$	0.006 <sub>0</sub>	0.005 <sub>2</sub>	$\text{CH}_3\text{CMe}=\text{CH}_2$	0.004 <sub>2</sub>
$\text{CH}_3\text{COF}$	0.004 <sub>7</sub>	0.005 <sub>5</sub>		
$\text{CH}_3\text{CONH}_2$		0.005 <sub>9</sub>		
$\text{CH}_3\text{COCN}$	0.005 <sub>5</sub>			

<sup>a</sup> Data from refs.<sup>4,14</sup>

<sup>b</sup> 4.21G basis set.<sup>16,56</sup>

$\Delta r_o$  (from  $\nu_{CH}^{is}$ ) values for some molecules chosen to illustrate two quite general chemical effects of CH bond strength variation.

TABLE II

 $\nu_{CH}^{is}$  and Bond Length Differences in Propane and Cyclohexane

$\nu_{CH}^{is}/\text{cm}^{-1}$	2950(s) <sup>a</sup>	2936(a) <sup>a</sup>	2923(eq) <sup>b</sup>	2981(ax) <sup>b</sup>
$\Delta r_o$ (pred.)/ $\text{\AA}$	0.001 <sub>4</sub> (a — s)		0.003 <sub>2</sub> (ax — eq)	
$\Delta r_o$ (calc.)/ $\text{\AA}$	0.000 <sub>7</sub> (a — s) <sup>c</sup>		0.001 <sub>7</sub> (ax — eq) <sup>c</sup>	

<sup>a</sup> Ref. [4], <sup>b</sup> ref. [19], <sup>c</sup> ref. [16], 4.21G basis set.

In the first series, a methyl group is attached to a C=C or C=O bond. Here the conformation taken up by the methyl group is such that two hydrogens H<sub>a</sub> lie above and below the skeletal plane of the molecule while the third, H<sub>s</sub> lies in this plane and *cis* to the C=X bond. In all cases the two methods agree very closely in making CH<sub>a</sub> bonds longer by 0.004—0.006 Å than the CH<sub>s</sub> ones. Conventional wisdom would ascribe this effect to hyperconjugation, although the author doubts whether this term describes the physical origin of the phenomenon in any real sense. Table II illustrates for the cases of propane and cyclohexane an effect which is general in saturated hydrocarbons, namely that in a given CH<sub>2</sub> or CH<sub>3</sub> group, a CH bond which lies *trans* (antiperiplanar) to another methyl group or CH<sub>2</sub> group lying  $\beta$  to it, is always stronger than one lying *trans* to a CH bond. Thus the in-plane CH<sub>s</sub> bond in the methyl group of propane is 15 cm<sup>-1</sup> stronger, or 0.0014 Å shorter than the CH<sub>a</sub> one.<sup>18</sup>

That the effect is cumulative, and roughly independent of whether a CH<sub>3</sub> or CH<sub>2</sub> group lies  $\beta$  to a CH bond, is shown by the example of cyclohexane. Here each axial CH bond lies *trans* to two CH bonds in the two neighbouring methylene groups, while each equatorial CH bond lies *trans* to two CH<sub>2</sub> groups. The observed  $\Delta \nu_{CH}^{is}$  (eq — ax) is 31 cm<sup>-1</sup>, just twice the difference in propane.<sup>19</sup> A particularly elegant illustration of the very close connection between  $\nu_{CH}^{is}$  values and 4—31G  $r_e$  CH ones in saturated compounds is found in a very recent work, which includes the  $\gamma$  effect of methyl groups, from a study of butane and pentane.<sup>20</sup>

In one sense, the *ab initio* results have made an indirect contribution to the correlation graph of Figure 4, in that they have helped to identify molecules where the CH bond lengths are poorly or wrongly determined by the rotational constant data (*e. g.* CH<sub>3</sub>OCH<sub>2</sub>X<sup>15</sup>) and which therefore ought not to be included in the correlation. As a corollary, one can say that the agreement between  $\nu_{CH}^{is}$  and *ab initio* results must now oblige microwave spectroscopists in particular to try even harder to remove from the rotational constants which they determine, the effects of the presence of zero point energy.

CORRELATION BETWEEN  $\nu$  AND HCH ANGLES

For methyl groups only, and ones which do not involve lone pair trans effects (this includes  $\text{CH}_3\text{F}$ )<sup>3</sup> there is a good correlation between  $\nu_{\text{CH}}^{\text{is}}$  and the HCH angle<sup>21</sup>:

$$\alpha \text{HCH} = 31.12 - 0.04709 \nu_{\text{CH}}^{\text{is}}$$

This works not only for symmetrical methyl groups, as in  $\text{CH}_3\text{X}$ , but also for some asymmetric ones e.g.  $\text{CH}_3\text{NO}_2$  and  $\text{CH}_3\text{BF}_2$  (see also below) as seen in Figure 5.

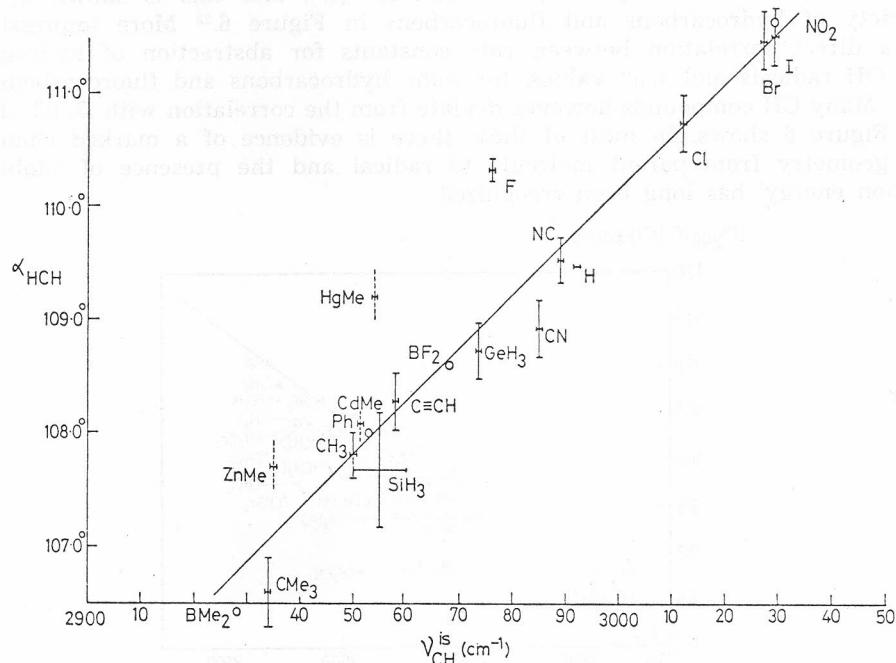


Figure 5. Correlation graph of  $\alpha \text{HCH}$  versus  $\nu_{\text{CH}}^{\text{is}}$ , data from refs. [21] and [44]

This has the interesting implication, that if for some reason the geometry of a methyl group could not be determined directly, a single, simple measurement of  $\nu_{\text{CH}}^{\text{is}}$  should allow prediction of both  $r_{\text{o}}\text{CH}$  and  $\alpha \text{HCH}$ , i.e. a completely determination of its geometry.

This possibility has recently been exploited in studies of organometallic compounds, including  $\text{CH}_3\text{M}(\text{CO})_5$  ( $\text{M}=\text{Mn, Re}$ ),<sup>22</sup>  $\text{CH}_3\text{CpM}(\text{CO})_3$  ( $\text{M}=\text{Cr, Mo, W; Cp = cyclopentadienyl}$ ),<sup>23</sup>  $(\text{CH}_3)_2\text{Cp}_2\text{M}$  ( $\text{M}=\text{Ti, Zr, Hf}$ )<sup>55</sup> and  $(\text{CH}_3)_3\text{M}$  ( $\text{M}=\text{Ga, Tl}$ ).<sup>47</sup>

There is of course a risk that a correlation established in one type of compound may not extend to another, and in this respect the angle/ $\nu_{\text{CH}}^{\text{is}}$  one could break down where the methyl group is attached to a metal atom, just as it does in molecules with lone pairs.

CORRELATION BETWEEN  $\nu_{\text{CH}}^{\text{is}}$  AND DISSOCIATION ENERGIES: EFFECTS ON REACTION RATES

It is one thing to correlate  $\nu_{\text{CH}}^{\text{is}}$  with a bond length, were both quantities describe the bond at equilibrium, but quite another, to expect a connection between  $\nu_{\text{CH}}^{\text{is}}$  and dissociation energy  $D_{\text{o}}$ (C—H), since the latter involves a difference between the energy at the potential minimum for the bond in the molecule, and the energy of the dissociated fragments. Chemical effects such as resonance may affect the energy of the radical formed which cannot operate in the parent molecule.<sup>24,57</sup> Nevertheless, there does appear to be a connection between the depth of the well, which is what  $D_{\text{o}}$ (C—H) is, and the curvature around  $r_{\text{e}}$ , which determines  $\nu_{\text{CH}}^{\text{is}}$ , and this is shown by a variety of hydrocarbons and fluorocarbons in Figure 6.<sup>25</sup> More impressive is a direct correlation between rate constants for abstraction of hydrogen by OH radicals and  $\nu_{\text{CH}}^{\text{is}}$  values, for some hydrocarbons and fluorocarbons.<sup>26</sup>

Many CH compounds however deviate from the correlation with  $D_{\text{o}}$ (C—H), as Figure 6 shows. In most of these there is evidence of a marked change of geometry from parent molecule to radical and the presence of 'stabilization energy' has long been recognized.

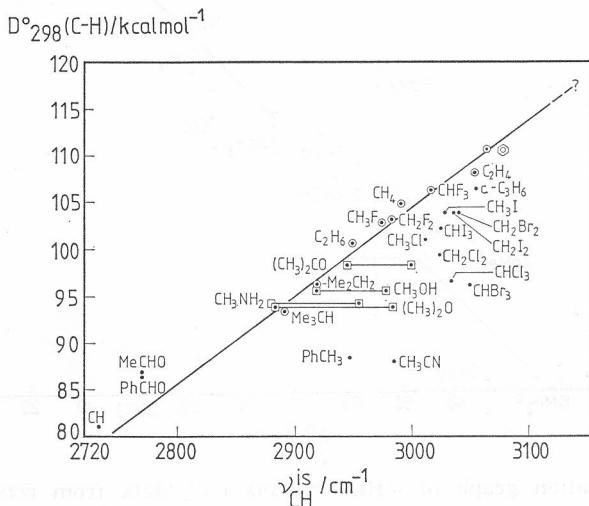


Figure 6. Correlation graph of  $D_{\text{o}}$ (C—H) versus  $\nu_{\text{CH}}^{\text{is}}$ , the line drawn being the best fit to hydro- and fluorocarbon data, denoted O. The pairs of points □—□ arise from the two  $\nu_{\text{CH}}^{\text{is}}$  values in each of the compounds  $\text{CH}_3\text{OH}$ ,  $(\text{CH}_3)_2\text{O}$ ,  $\text{CH}_3\text{NH}_2$  and  $(\text{CH}_3)_2\text{CO}$ . Points for acetylenic CH bonds probably lie below the line drawn. Data from ref. [12], updated in part. A further update incorporating new data will appear soon.<sup>57</sup>

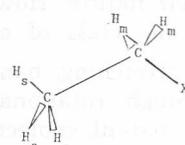
The most significant feature of the correlation plot is perhaps its gradient which is  $\sim 0.9 \text{ kcal mol}^{-1}$  per  $10 \text{ cm}^{-1}$  change in  $\nu_{\text{CH}}^{\text{is}}$ .<sup>12</sup> Applying this to the two kinds of bond in  $(\text{CH}_3)_3\text{N}$  we would predict a difference of  $\sim 13 \text{ kcal}$  between their  $D_{\text{o}}$  values. In kinetic terms, this is an enormous effect, but for it to be manifest, the dissociation process would have to be an adiabatic one, taking place along the equilibrium direction of the bond concerned. If the hydrogen were abstracted by an incoming species the trajectory and duration of the collision would have to be such that no

rotation of the methyl group occurred during the formation of the  $\text{CH}_2\text{N}(\text{CH}_3)_2$  radical.

There is in fact one slight piece of evidence to suggest that in actual dissociation processes, observed kinetically, for methyl groups containing two kinds of CH bond, that it is indeed the weak bond which is dissociating. For  $\text{CH}_3\text{OH}$ ,  $\text{CH}_3\text{NH}_2$ ,  $(\text{CH}_3)_2\text{O}$  and  $(\text{CH}_3)_2\text{CO}$  there is one measured dissociation energy, but two  $\nu_{\text{CH}}^{is}$  values, for the strong and weak bonds respectively. Plotting two points, then, for each molecule, we find the point for the lower  $\nu_{\text{CH}}^{is}$  value lying closer to the correlation line than that for the higher value. Clearly a kinetic determination of  $D_0(\text{C}-\text{H})$  in  $(\text{CH}_3)_3\text{N}$  would be of great interest.\*

A rather smaller difference in bond strength would be predicted for the axial and equatorial bonds in cyclohexane (2.8 kcal) but this is enough to warrant an examination of its contribution first to the relative reactivities of the two kinds of bond and secondly to the relative stabilities of the conformers of substituted cyclohexanes in addition to the effects usually considered.<sup>27</sup> Similar considerations apply to the elimination of  $\text{HX}$  from ethyl halides. As shown in Table III, a CH bond in the methyl group *trans* to the CX bond is consistently weaker than one *gauche* to the latter, and this factor favours the preferred '*trans*' elimination. Again, this is an effect not previously taken into account.<sup>28</sup> The data here also show a striking difference in behaviour of the two kinds of bond when the halogen is varied. The *gauche* bond is essentially unaffected: the *trans* CH bond weakens in the sequence  $\text{F} > \text{Cl} > \text{Br} > \text{I}$ .

TABLE III

 $\nu_{\text{CH}}^{is}$  Values in Ethyl Compounds<sup>a</sup>

$X =$	F	Cl	Br	I	H	$\text{CH}_3$
$\text{H}_m$	2950	2983	2996	2998	2936	2920
$\text{H}_s$	2957	2945	2936	2928	2950	2950
$\text{H}_a$	2973	2972	2971	2969	2950	2936

<sup>a</sup> Data from reference [4].

Table III also includes data for the CH bond  $\alpha$  to the halogen in ethyl halides. There is clearly no simple inductive effect operating here (methyl halides behave similarly<sup>4</sup>).

#### COMPARISON OF $\nu_{\text{CH}}^{is}$ AND LOCAL' MODE' STUDIES

By 'local mode' study, is understood the measurement in the near infrared and visible regions of the spectrum of bands due to high overtones of CH stretching vibrations in normal, undeuterated molecules. These have been shown to characterise individual CH oscillators in situations where

\* This is now available.

groups of CH bonds are present.<sup>29</sup> Frequencies of a series of overtone bands lead to values both of the mechanical or harmonic frequency  $\omega_i$  of the vibrating bond and of its anharmonicity  $X_i$ . The causes of this phenomenon have been discussed elsewhere extensively<sup>29,30</sup> and need not concern us here. The point to make is that here is an alternative route to a measurement of the 'equilibrium' strength of individual CH bonds, and the relative merits of the two methods should be discussed.

The local mode approach has one great advantage — there is usually no need to partially deuteriate the molecule concerned. This is particularly important in the case of aromatic compounds where the problems of synthesizing partially deuterated species are immense. Some elegant studies by Gough and Henry on methyl<sup>31</sup> and fluorinated benzenes<sup>32</sup> however, using comparatively unsophisticated equipment, have shown the power of the method, and demonstrated further the close relation between CH frequency changes, and bond length variations calculated *ab initio*. A further study by these authors of nitrobenzene shows however that partial deuteration may be necessary to identify with certainty the bonds involved.<sup>33</sup>

This problem of band assignment in fact constitutes the main drawback to the 'local mode' approach. It is rare for the high overtone bands to exhibit rotational contours from which the directions of the bonds concerned may be deduced. In their absence, the only aids to assignment are

- (1) comparison with *ab initio*  $\Delta r_e$  calculations, already validated by the  $\nu_{CH}^{is}$  work;
- (2) the assumption that overtone intensities depend only on the numbers of CH bonds, and not on their nature. However this assumption is known to break down in at least one class of compound,  $CH_3-C=O$  ones.<sup>34,56</sup>

By contrast, 'isolated' CH stretching bands in the fundamental region can be assigned, not only through rotational contours, but also by their relation to the bands of their parent molecules. This is discussed further below.

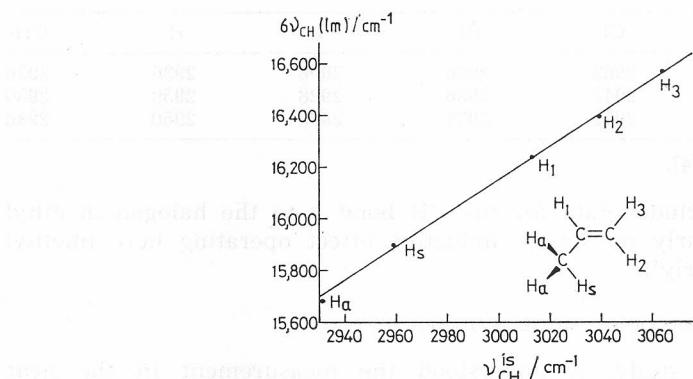


Fig. 7.  $6\nu_{CH}$  (local mode, overtone)<sup>35</sup> plotted against  $\nu_{CH}^{is}$ <sup>4</sup> for the five CH bonds in propene. Care has to be taken in determining  $\nu_{CH}^{is}$  values for  $C=C-H$  system since Fermi resonances between  $\nu C-H$  and  $\nu C=C+\delta CH$  combinations may be present in the partially deuterated species as well as in the parent molecules.

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What is most welcome to find, however, is the agreement between the two methods, applied to the same molecule. A direct and precise correlation between the fifth overtone, local mode frequency and  $\nu_{\text{CH}}^{\text{is}}$  was found by Wong and Moore for a series of hydrocarbons<sup>35</sup> the data for one of which, propene, are displayed in Figure 7. Five different CH bonds are present in this molecule, three olefinic and two in the methyl group. The olefinic ones incidentally show effects similar to those in saturated compounds. The bond CH<sup>3</sup> which is *trans* to methyl is stronger than the one CH<sup>2</sup>, which is *cis* to methyl, while by far the weakest of the three is bond CH<sup>1</sup>, which is  $\alpha$  to methyl, in agreement with the  $\alpha_{\text{Me}}$  effect seen in the series Me—H (2992), MeCH<sub>3</sub> (2950), Me<sub>2</sub>CH<sub>2</sub> (2920), Me<sub>3</sub>CH (2892).<sup>4</sup> The same order of strength for the bonds in propene is obtained if the local mode  $\omega_{\text{CH}}$  value, derived from an overtone progression, is compared with  $\nu_{\text{CH}}^{\text{is}}$ , but the quantitative comparison is somewhat disappointing.<sup>36</sup> The same differing *cis* and *trans* effects of methyl combine to render the olefinic bond in *cis* but-2-ene stronger than that in *trans* but-2-ene by about 26 cm<sup>-1</sup>.<sup>37</sup> Elsewhere, the earlier diagnosis of CH bond strength differences in the methyl groups of CH<sub>3</sub>—N and CH<sub>3</sub>—O compounds have all recently been confirmed by local mode studies.<sup>38,39</sup>

#### UNDERSTANDING THE CH STRETCHING REGION

Isolated CH stretching frequencies not only provide information about the strengths of individual CH bonds, they also constitute a key to the understanding of the spectra of the parent molecules. Conversely, the latter can be used in assigning  $\nu_{\text{CH}}^{\text{is}}$  bands in certain circumstances.

The spectra of 'isolated' CH<sub>3</sub> and CH<sub>2</sub> groups will be considered first. Here the major problem is to assess the degree of Fermi resonance affecting the CH stretching fundamentals. Since, normally, the major effect is on  $\nu_s$  levels, this may be estimated very simply by use of the approximate sum rule for CH stretching motions,

$$\sum \nu_i \text{CH}_3/\text{CH}_2 = \sum_i \nu_{\text{CH}}^{\text{is}}$$

where each CH<sub>3</sub> group has three frequencies and each CH<sub>2</sub> group, two, and the  $\nu_{\text{CH}}^{\text{is}}$  sum is over all CH bonds present.<sup>40</sup> For example, observation of  $\nu_{\text{as}}$  CH<sub>3</sub> and  $\nu_{\text{CH}}^{\text{is}}$  in CH<sub>3</sub>Cl at 3039.25 and 3012.2 cm<sup>-1</sup> respectively<sup>41</sup> yields a value of  $\nu_s^\circ \text{CH}_3 = 3 \times 3012.2 - 2 \times 3039.25 = 2958.1 \text{ cm}^{-1}$  which is close to the values of 2952 cm<sup>-1</sup> obtained from an accurate W value of 34 cm<sup>-1</sup>.<sup>42</sup>

A slightly more sophisticated approach is a normal coordinate treatment, on an internal coordinate basis, of the CH and CD stretching motions, in isolation from all others on the molecule — an example of an 'energy factored' force field, more familiar when applied to carbonyl stretching vibrations in organometallic compounds. Applied to a methyl group, this has been called a '3 × 3' force constant refinement. This tends to give slightly larger Fermi resonance shifts than the sum rule.<sup>41</sup> It also has the merit of yielding both diagonal and interaction stretch-stretch force constants, and is particularly important when applied to methyl groups with bonds of differing strength. The local symmetry of the group is then reduced to C<sub>s</sub> or lower, in the former case leading to two a' and one a'' stretching

vibrations, instead of  $\nu_{as}$  and  $\nu_s$  ones. A splitting of  $\nu_{as}\text{CH}_3$  into  $a'$  and  $a''$  modes is indeed observed in every case where two  $\nu\text{CHD}_2$  bands are observed and obeys the following rule:  $\nu_{as}(a') > \nu_{as}(a'')$  for two weak and one strong CH bands, and *vice versa* [cf. 14]. Thus a diagnosis of the number of weak and strong bonds in the methyl group (and hence assignment of the  $\text{CHD}_2$  spectrum) can be made simply by identifying the symmetries of the split  $\nu_{as}\text{CH}_3$  modes. A wrong assignment shows up through anomalous interaction force constants emerging from the refinement. These constants are normally around 0.03 mdyn/ $\text{\AA}$  in size.

In many molecules of course  $\text{CH}_3$  or  $\text{CH}_2$  groups are not isolated. Within the approximation that bending motions are ignored, the only additional problem molecules such as ethyl halides present is the magnitude of the interaction stretching force constants between CH bonds  $\beta$  or  $\gamma$  to each other. This is because there are no kinetic energy terms linking these motions, since there are no atoms common to the two CH bonds involved. So far as is known, the  $\gamma$  interactions are negligible, but the  $\beta$  constants not so, values of  $f'$  up to 0.03 mdyn/ $\text{\AA}$  being not uncommon, with differing signs depending on whether the CH bonds are *gauche* or *trans* to each other.<sup>43</sup> The changes of  $\nu\text{CH}$  due to these interactions are small, being largest, up to about 10  $\text{cm}^{-1}$ , where the individual bonds have identical frequencies. Coupling effects of this order are unlikely to show up in complete normal coordinate treatments of molecular vibrations, and an 'energy factored' approach utilising  $\nu_{\text{CH}}^{\text{is}}$  data is necessary to reveal them.

A final note of caution is needed regarding the handling of  $\nu\text{CD}$  data. The high anharmonicity associated with CH stretching means that observed  $\nu\text{CH}$  and  $\nu\text{CD}$  frequencies are to some extent incompatible. A convenient device for overcoming this in a  $3 \times 3$  refinement is to divide all observed  $\nu\text{CD}$  frequencies by the empirical factor 1.011.<sup>41</sup> Three other factors render  $\nu_{\text{CD}}^{\text{is}}$  values less valuable than  $\nu_{\text{CH}}^{\text{is}}$  ones. Firstly, they lie in a region which contains a higher proportion of overtone and combination bands not necessarily associated with *e.g.*  $\delta_a\text{CD}_3$  or  $\delta_s\text{CD}_3$  modes. Secondly, the effect of the latter can be quite different to what is found in the  $\nu\text{CH}$  region. Thus in many molecules  $2\delta_s\text{CD}_3$  bands lie *above*, but  $2\delta_{as}\text{CD}_3$  ones *below*, the  $\nu\text{CD}$  bands. Thirdly, the lower CD stretching vibrations involve higher proportions of bending and other motions and so are less 'isolated' than their CH counterparts.

#### $\nu_{\text{CH}}^{\text{is}}$ AND INTERNAL ROTATION OF METHYL GROUPS

All the cases of differing CH bond strength within methyl groups listed above have involved sizable barriers ( $\sim 2$  kcal  $\text{mol}^{-1}$ ) to internal rotation. When such barriers become very low, as in  $\text{ZnMe}_2$ ,  $\text{MeNO}_2$ ,  $\text{MePh}$  and  $\text{MeBF}_2$  ( $1-5$   $\text{cm}^{-1}$ ), various unusual effects in the  $\nu\text{CH}$  spectrum are seen. In zinc dimethyl, the  $\text{CHD}_2$  spectrum consists of a hybrid band of which a parallel component (PQR type) derives from the component of  $(\partial\mu/\partial r)$  CH along the C—Zn axis, and a perpendicular one (succession of Q branches) from the component of  $(\partial\mu/\partial r)$  CH perpendicular to that axis, the Q branch spacing being characteristic of a single freely rotating  $\text{CHD}_2$  group.<sup>44</sup> There is no hint of any CH force constant variation during internal rotation. By contrast, in  $\text{MeNO}_2$ ,  $\text{MePH}$ ,  $\text{Me}_3\text{B}$ ,  $\text{MeBF}_2$  and  $\text{MeBCl}_2$  varying effects

are seen which can only be accounted for in the terms of a freely rotating methyl group in which however the CH force constant varies during the rotation, such that the bond is strongest in the skeletal plane of the molecule, weakest at right angles to this plane.<sup>4,45</sup> This variation effectively creates a barrier in the upper CH stretching vibrational state, even though the barrier in the ground state, due to conventional steric effects, is negligible.<sup>45</sup> Again there is *ab initio* evidence to support this interpretation.<sup>4,45</sup> More recently, the same effects have been observed in Me<sub>3</sub>Ga and Me<sub>3</sub>Tl.<sup>46,47</sup>

A similar CH force constant variation has been postulated in MeMn(CO)<sub>5</sub> and MeRe(CO)<sub>5</sub> to explain the spectra seen, although in these cases there is no evidence as to which direction the bond is strongest in.<sup>22</sup>

#### OTHER TYPES OF MH BOND

Nearly all the chemical effects found amongst CH bonds are found in some measure at least in other types of bond as well. Thus lone pair *trans* effects have been found for NH<sup>48</sup>, SiH<sup>5</sup> and GeH<sup>49</sup> bonds. The  $\beta$  effect of a methyl group is also common to CH, SiH<sup>50</sup>, GeH<sup>49</sup> and SnH<sup>51</sup> bonds and this has interesting implications for distinguishing between conformers. One significant chemical difference however between CH bonds in a methyl group, and SiH ones in a SiH<sub>3</sub> one, is the effect of a vinyl group. This does not appear to weaken the SiH<sub>a</sub> bond in CH<sub>2</sub>=CHSiH<sub>3</sub> the way it does the CH<sub>a</sub> bond in CH<sub>2</sub>=CHCH<sub>3</sub>.<sup>50</sup> A novel feature of SiH and GeH containing molecules is a form of 'local mode' behaviour in the *undeuterated* compound, in the *fundamental* region.<sup>49,50</sup> Also of potential value in the case of MH bonds, where M is heavier than carbon, is the use of overtone frequencies of  $\nu_{MH}^{is}$  bands to yield anharmonicities and estimates of  $D_o(M-H)$ .<sup>52,53</sup> The correlation between  $r_o$ SiH and  $\nu^{is}_{SiH}$  values is not as good as that involving CH bonds.<sup>54</sup>

#### CONCLUSION

It is hoped that the present survey will leave the reader with some impression of the richness and range of the variations in CH bond strength that have been found during the last 15 years by three separate techniques, partial deuteration, 'local mode' and *ab initio* studies, of which the first is best suited to explain the familiar but complicated spectra found in the CH stretching regions of the spectra of organic and organometallic compounds.

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### SAŽETAK

**Interpretacija područja CH rastezanja s pomoću infracrvenih spektara djelomično deuteriranih spojeva**

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Dan je pregled informacija izvedenih iz proučavanja frekvencija rastezanja CH veza, koje su određene za djelomično deuterirane organske i organometalne spojeve. Podaci se odnose na duljine veza CH i disocijacijske energije, te kuteve HCH u metilnim skupinama. Utvrđeno je odlično slaganje između razlika duljina veza predviđenih iz vrijednosti  $\nu_{\text{CH}}^{\text{1s}}$  i onih proračunanih *ab initio* metodama. Podaci o  $\nu_{\text{CH}}^{\text{1s}}$  slažu se i s rezultatima o višim gornjim tonovima, studiju lokalnih načina vibracije za utvrđivanje razlika u jakosti veza CH. Prethodni se podaci temelje na spektrima, koji se lakše mogu pripisati određenim vezama. Oni olakšavaju i razumijevanje spektara normalnih, nedeuteriranih molekula u području rastezanja veza CH uz pomoć računa »energijski faktoriziranog polja sila«.

Navedeni su slučajevi sa slobodnim metilnim skupinama, te s drugim »izoliranim« vezama MH (M=N, Si, Ge, Sn).