

CCA-1805

YU ISSN 0011-1643

UDC 543.42

Author's Review

Interpreting the CH Stretching Region, Through Infrared Partial Deuteration Studies

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Received Juni 5, 1987

Information derived from a study of 'isolated' CH stretching frequencies, measured in partially deuterated organic and organo-metallic 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 $\nu_{\text{CH}}^{\text{is}}$ values and those calculated by *ab initio* methods. $\nu_{\text{CH}}^{\text{is}}$ 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 Martin¹ 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 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.²

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 CH_3Cl , 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 cm^{-1} , while a Fermi resonance between the upper vibrational level of the ν_s band and the $\nu_5 = 2$ 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.

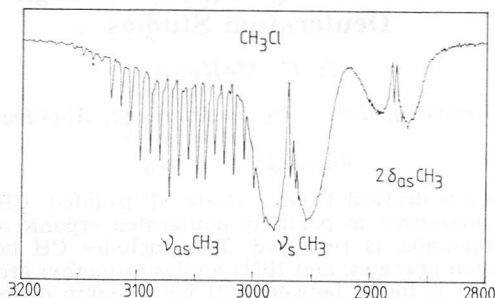


Figure 1. Infrared spectrum of CH_3Cl vapour, showing 3 bands, due to $\nu_{as} \text{CH}_3$, $\nu_s \text{CH}_3$ and $2\delta_{as} \text{CH}_3$ respectively, the latter two in Fermi resonance with each other.

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 CHD_2Cl , Figure 2, just one νCH band is seen in the 3000 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 νCH one, and secondly, the δCH modes occur near 1300 cm^{-1} and their overtones are not significantly in resonance with νCH .

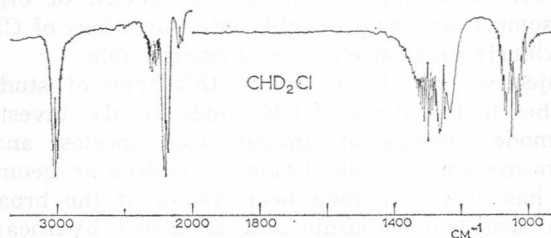


Figure 2. Infrared spectrum of CHD_2Cl vapour, showing a solitary νCH band at 3012 cm^{-1} , two νCD bands near 2200 cm^{-1} and δCH bands near 1300 cm^{-1} .⁵ (Reprinted by permission from *J. Mol. Struct.*¹⁶).

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.³ A major review of the work in the 70's appeared in 1978,⁴ and a minor one mainly relating to GeH and SiH bonds in 1984.⁵

One of the most pleasing results of the partial deuteration experiment is the appearance of several bands in the ν 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 CHD_2 substituted methylamines in which the mono and trimethyl compounds each exhibit two ν 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.

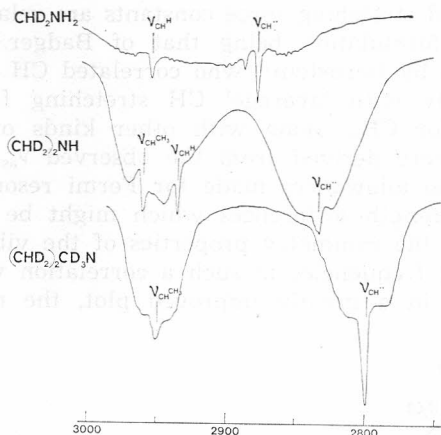


Figure 3. Infrared spectra of CHD_2 labelled methylamines, showing the presence of different types of CH bond, the weakest in each case due to the bond *trans* (anti periplanar) to the lone pair of electrons (CH^-). The rotational contours help to identify the bonds concerned.⁵ (Reprinted by permission from *J. Mol. Struct.*¹⁰)

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.⁶ The existence of an effect peculiar to this bond has long been known⁷ and is linked with other effects such as the '*anomeric*' one.⁸ 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 cm^{-1} ,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.⁹

To return to the 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 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)

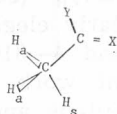
of which is shown in Figure 4.⁵ It has first to be said that the positions of hydrogen atoms in molecules are notoriously difficult to pinpoint by experimental means. Due to the presence of zero point energy of vibration, each type of experiment — spectroscopic, electron or X-ray diffraction, yields 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.¹³ Two molecules are of special interest here, Me_3N and Me_2O . 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 ν_{CH}^{is} values, and the two pairs of points then lie very close to the overall correlation curve. The 150 cm^{-1} difference in ν_{CH}^{is} in Me_3N indicates then an r_o CH difference of 0.015 \AA — a change whose significance can be brought out as follows. A change in ν_{CH}^{is} of 10 cm^{-1} corresponds to a Δr_o CH value of 0.001 \AA . The effects of coupling *etc.* on ν_{CH}^{is} in similar molecules probably introduces an uncertainty of the order of 5 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 ν_{CH}^{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 ν_{CH}^{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 ν_{CH}^{is} .⁴ Nevertheless the changes from one bond to another in Δr_e and Δr_o should run parallel, and this is indeed found.^{16,17} Tables I and II compare Δr_e (*ab initio*) and

TABLE I

CH Bond Length Differences Within Methyl Groups Attached to Double Bonds



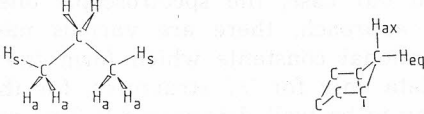
| | $\Delta r_{CH} (a - s)/\text{\AA}$ | | | $\Delta r_{CH} (a - s)/\text{\AA}$ | |
|--------------|------------------------------------|-----------------------------|----------------|------------------------------------|-----------------------------|
| | ν_{CH}^{is} ^a | <i>ab. in.</i> ^b | | ν_{CH}^{is} ^a | <i>ab. in.</i> ^b |
| CH_3CHO | 0.005 ₉ | 0.005 ₄ | $CH_3CH=CH_2$ | 0.002 ₉ | 0.002 ₇ |
| CH_3COMe | 0.006 ₀ | 0.005 ₂ | $CH_3CMe=CH_2$ | 0.004 ₂ | 0.003 ₉ |
| CH_3COF | 0.004 ₇ | 0.005 ₃ | | | |
| CH_3CONH_2 | | 0.005 ₉ | | | |
| CH_3COCN | 0.005 ₃ | | | | |

^a Data from refs. 4, 14.

^b 4.21G basis set.^{16,56}

Δr_o (from ν_{CH}^{is}) values for some molecules chosen to illustrate two quite general chemical effects of CH bond strength variation.

TABLE II
 ν_{CH}^{is} and Bond Length Differences in Propane and Cyclohexane



| $\nu_{CH}^{is}/\text{cm}^{-1}$ | 2950(s) ^a | 2936(a) ^a | 2923(eq) ^b | 2981(ax) ^b |
|--------------------------------|---|----------------------|---|-----------------------|
| Δr_o (pred.)/Å | 0.001 ₄ (a — s) | | 0.003 ₂ (ax — eq) | |
| Δr_e (calc.)/Å | 0.000 ₇ (a — s) ^c | | 0.001 ₇ (ax — eq) ^c | |

^a Ref. [4], ^b ref. [19], ^c 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_a lie above and below the skeletal plane of the molecule while the third, H_s lies in this plane and *cis* to the C=X bond. In all cases the two methods agree very closely in making CH_a bonds longer by 0.004–0.006 Å than the CH_s 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_2 or CH_3 group, a CH bond which lies *trans* (antiperiplanar) to another methyl group or CH_2 group lying β to it, is always stronger than one lying *trans* to a CH bond. Thus the in-plane CH_s bond in the methyl group of propane is 15 cm^{-1} stronger, or 0.0014 Å shorter than the CH_a one.¹⁸

That the effect is cumulative, and roughly independent of whether a CH_3 or CH_2 group lies β 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_2 groups. The observed $\Delta \nu_{CH}^{is}$ (eq — ax) is 31 cm^{-1} , just twice the difference in propane.¹⁹ A particularly elegant illustration of the very close connection between ν_{CH}^{is} values and 4–31G r_e CH ones in saturated compounds is found in a very recent work, which includes the γ effect of methyl groups, from a study of butane and pentane.²⁰

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_3OCH_2X ¹⁵) and which therefore ought not to be included in the correlation. As a corollary, one can say that the agreement between ν_{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 ν AND HCH ANGLES

For methyl groups only, and ones which do not involve lone pair trans effects (this includes CH_3F !)³) there is a good correlation between $\nu_{\text{CH}}^{\text{is}}$ and the HCH angle²¹:

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

This works not only for symmetrical methyl groups, as in CH_3X , but also for some asymmetric ones *e.g.* CH_3NO_2 and CH_3BF_2 (see also below) as seen in Figure 5.

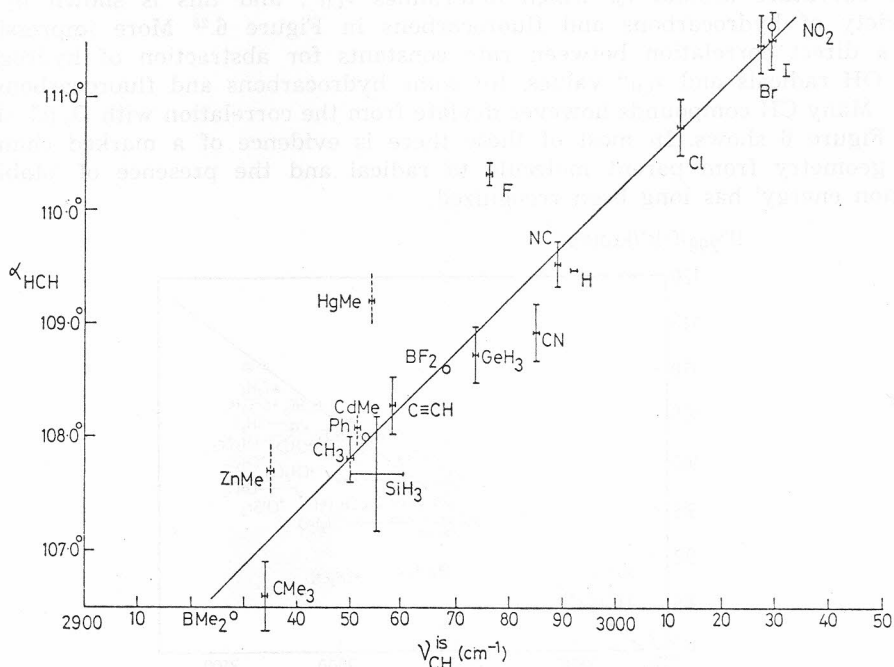


Figure 5. Correlation graph of αHCH versus $\nu_{\text{CH}}^{\text{is}}$, data from refs. [21] and [44]

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_{CH} and αHCH , *i.e.* a complete determination of its geometry.

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

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 $D_0(\text{C—H})$, 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.^{24,57} Nevertheless, there does appear to be a connection between the depth of the well, which is what $D_0(\text{C—H})$ is, and the curvature around r_e , which determines $\nu_{\text{CH}}^{\text{is}}$, and this is shown by a variety of hydrocarbons and fluorocarbons in Figure 6.²⁵ 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.²⁶

Many CH compounds however deviate from the correlation with $D_0(\text{C—H})$, 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.

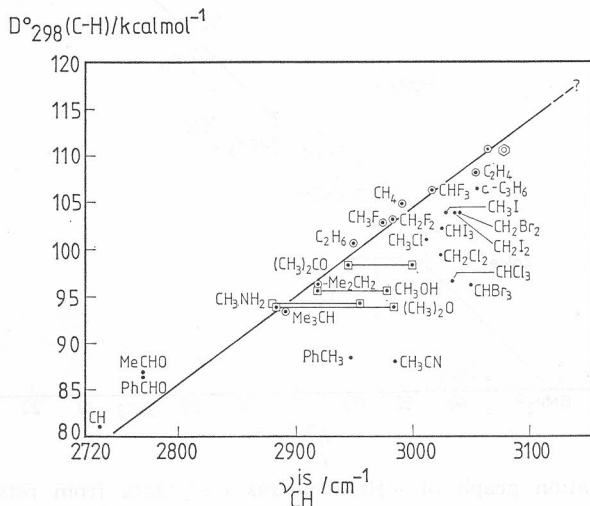


Figure 6. Correlation graph of $D_0(\text{C—H})$ versus $\nu_{\text{CH}}^{\text{is}}$, the line drawn being the best fit to hydro- and fluorocarbon data, denoted O. The pairs of points \square — \square arise from the two $\nu_{\text{CH}}^{\text{is}}$ values in each of the compounds CH_3OH , $(\text{CH}_3)_2\text{O}$, CH_3NH_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.⁵⁷

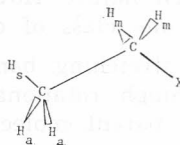
The most significant feature of the correlation plot is perhaps its gradient which is ~ 0.9 kcal mol⁻¹ per 10 cm⁻¹ change in $\nu_{\text{CH}}^{\text{is}}$.¹² Applying this to the two kinds of bond in $(\text{CH}_3)_3\text{N}$ we would predict a difference of ~ 13 kcal between their D_0 values. In kinetic 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 CH_3OH , CH_3NH_2 , $(\text{CH}_3)_2\text{O}$ and $(\text{CH}_3)_2\text{CO}$ there is one measured dissociation energy, but two $\nu_{\text{CH}}^{\text{is}}$ values, for the strong and weak bonds respectively. Plotting two points, then, for each molecule, we find the point for the lower $\nu_{\text{CH}}^{\text{is}}$ 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.²⁷ Similar considerations apply to the elimination of 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.²⁸ 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

 $\nu_{\text{CH}}^{\text{is}}$ Values in Ethyl Compounds^a

| X = | F | Cl | Br | I | H | CH ₃ |
|----------------|------|------|------|------|------|-----------------|
| H _m | 2950 | 2983 | 2996 | 2998 | 2936 | 2920 |
| H _s | 2957 | 2945 | 2936 | 2928 | 2950 | 2950 |
| H _a | 2973 | 2972 | 2971 | 2969 | 2950 | 2936 |

^a Data from reference [4].

Table III also includes data for the CH bond α to the halogen in ethyl halides. There is clearly no simple inductive effect operating here (methyl halides behave similarly⁴).

COMPARISON OF $\nu_{\text{CH}}^{\text{is}}$ 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.²⁹ Frequencies of a series of overtone bands lead to values both of the mechanical or harmonic frequency ω_i of the vibrating bond and of its anharmonicity X_i . The causes of this phenomenon have been discussed elsewhere extensively^{29,30} 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 deuterate 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 methyl³¹ and fluorinated benzenes³² 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.³³

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* Δr_e calculations, already validated by the $\nu_{\text{CH}}^{\text{is}}$ 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, $\text{CH}_3\text{—C=O}$ ones.^{34,56}

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.

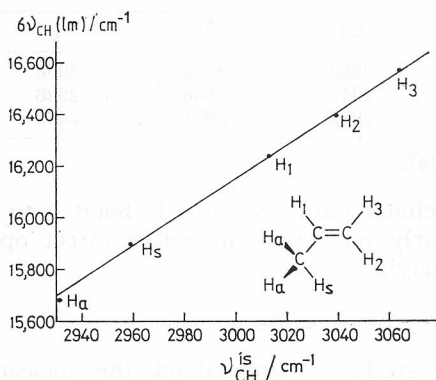


Fig. 7. $6\nu_{\text{CH}}$ (local mode, overtone)³⁵ plotted against $\nu_{\text{CH}}^{\text{is}}$ ⁴ for the five CH bonds in propene. Care has to be taken in determining $\nu_{\text{CH}}^{\text{is}}$ values for C=C—H system since Fermi resonances between $\nu_{\text{C—H}}$ and $\nu_{\text{C=C}} + \delta_{\text{CH}}$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

Reprinted by permission from *J. Mol. Structure*.⁵

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 hydrocarbons³⁵ 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^3 which is *trans* to methyl is stronger than the one CH^2 , which is *cis* to methyl, while by far the weakest of the three is bond CH^1 , which is α to methyl, in agreement with the α_{Me} effect seen in the series Me-H (2992), MeCH_3 (2950), Me_2CH_2 (2920), Me_3CH (2892).⁴ The same order of strength for the bonds in propene is obtained if the local mode ω_{CH} value, derived from an overtone progression, is compared with $\nu_{\text{CH}}^{\text{is}}$, but the quantitative comparison is somewhat disappointing.³⁶ 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^{-1} .³⁷ Elsewhere, the earlier diagnosis of CH bond strength differences in the methyl groups of $\text{CH}_3\text{-N}$ and $\text{CH}_3\text{-O}$ compounds have all recently been confirmed by local mode studies.^{38,39}

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_3 and CH_2 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 ν_s levels, this may be estimated very simply by use of the approximate sum rule for CH stretching motions,

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

where each CH_3 group has three frequencies and each CH_2 group, two, and the $\nu_{\text{CH}}^{\text{is}}$ sum is over all CH bonds present.⁴⁰ For example, observation of $\nu_{\text{as}}\text{CH}_3$ and $\nu_{\text{CH}}^{\text{is}}$ in CH_3Cl at 3039.25 and 3012.2 cm^{-1} respectively⁴¹ 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^{-1} obtained from an accurate W value of 34 cm^{-1} .⁴²

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.⁴¹ 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_s or lower, in the former case leading to two a' and one a'' stretching

vibrations, instead of ν_{as} and ν_s ones. A splitting of ν_{as} CH₃ into a' and a'' modes is indeed observed in every case where two ν CHD₂ 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 CHD₂ spectrum) can be made simply by identifying the symmetries of the split ν_{as} CH₃ modes. A wrong assignment shows up through anomalous interaction force constants emerging from the refinement. These constants are normally around 0.03 mdyn/Å in size.

In many molecules of course CH₃ or CH₂ 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 β or γ 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 γ interactions are negligible, but the β constants not so, values of f' up to 0.03 mdyn/Å being not uncommon, with differing signs depending on whether the CH bonds are *gauche* or *trans* to each other.⁴³ The changes of ν CH due to these interactions are small, being largest, up to about 10 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 ν_{CH}^{is} data is necessary to reveal them.

A final note of caution is needed regarding the handling of ν CD data. The high anharmonicity associated with CH stretching means that observed ν CH and ν CD frequencies are to some extent incompatible. A convenient device for overcoming this in a 3 × 3 refinement is to divide all observed ν CD frequencies by the empirical factor 1.011.⁴¹ Three other factors render ν_{CD}^{is} values less valuable than ν_{CH}^{is} ones. Firstly, they lie in a region which contains a higher proportion of overtone and combination bands not necessarily associated with *e.g.* δ_a CD₃ or δ_s CD₃ modes. Secondly, the effect of the latter can be quite different to what is found in the ν CH region. Thus in many molecules 2 δ_s CD₃ bands lie *above*, but 2 δ_{as} CD₃ ones *below*, the ν 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.

ν_{CH}^{is} AND INTERNAL ROTATION OF METHYL GROUPS

All the cases of differing CH bond strength within methyl groups listed above have involved sizable barriers (~ 2 kcal mol⁻¹) to internal rotation. When such barriers become very low, as in ZnMe₂, MeNO₂, MePh and MeBF₂ (1–5 cm⁻¹), various unusual effects in the ν CH spectrum are seen. In zinc dimethyl, the CHD₂ 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 CHD₂ group.⁴⁴ There is no hint of any CH force constant variation during internal rotation. By contrast, in MeNO₂, MePh, Me₃B, MeBF₂ and MeBCl₂ 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.^{4,45} 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.⁴⁵ Again there is *ab initio* evidence to support this interpretation.^{4,45} More recently, the same effects have been observed in Me₃Ga and Me₃Tl.^{46,47}

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

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 NH⁴⁸, SiH⁵ and GeH⁴⁹ bonds. The β effect of a methyl group is also common to CH, SiH⁵⁰, GeH⁴⁹ and SnH⁵¹ 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 SiH₃ one, is the effect of a vinyl group. This does not appear to weaken the SiH_a bond in CH₂=CHSiH₃ the way it does the CH_a bond in CH₂=CHCH₃.⁵⁰ A novel feature of SiH and GeH containing molecules is a form of 'local mode' behaviour in the *undeuterated* compound, in the *fundamental* region.^{49,50} Also of potential value in the case of MH bonds, where M is heavier than carbon, is the use of overtone frequencies of ν_{MH}^{18} bands to yield anharmonicities and estimates of $D_0(M-H)$.^{52,53} The correlation between r_0 SiH and ν^{18}_{SiH} values is not as good as that involving CH bonds.⁵⁴

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 $\nu_{\text{CH}}^{\text{is}}$ i onih proračunanih *ab initio* metodama. Podaci o $\nu_{\text{CH}}^{\text{is}}$ 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).