# CH STRETCHING FREQUENCIES AND BOND STRENGTHS, AND METHYL GROUP GEOMETRY IN $CH_3CXO$ COMPOUNDS (X = H, Me, F, Cl, Br, I, CN, OMe) AND $CH_3CH_2CN$

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#### ABSTRACT

Infrared spectra in the CH stretching region are reported for CHD<sub>2</sub>CXO and CH<sub>3</sub>CXO compounds, where X = F, Cl, Br, I, CN, OMe, and for CHD<sub>2</sub>CD<sub>2</sub>CN and CD<sub>3</sub>CHDCN. In all the carbonyl compounds except the iodide the two out-of-plane CH bonds in the methyl group are significantly weaker than the in-plane one. Differences in CH bond length of up to 0.006 Å are predicted, which are considered to be more reliable than the available microwave data. The separations of  $\nu_{as}$ CH<sub>3</sub> and  $\nu$ CHD, frequencies are compatible with a strong angular asymmetry ( $\angle H_s$ CH<sub>a</sub>  $\neq \angle H_a$ CH<sub>a</sub>) in the acetyl compounds. The gauche and trans effects of halogen on  $\nu_{CH}^{is}$  are similar, but larger, than those in alkyl halides. In ethyl cyanide, the methyl CH bonds are identical in strength. The  $\alpha$  and  $\beta$  substituent effects from the CN group fall into no simple pattern.

## INTRODUCTION

The presence of two weak out-of-plane and one strong in-plane CH bonds in the methyl groups of acetaldehyde and acetone has previously been demonstrated by the partial deuteration CH stretching frequency method [1]. The  $v_{CH}^{is}$  values found in the CHD<sub>2</sub> groups give quantitative information about the strength of the CH bond, and in particular about the bond length, information which is very difficult to obtain from experimental studies involving microwave spectroscopy or electron diffraction. That variations in  $v_{CH}^{is}$  truly reflect variations in  $r_e$  is suggested strongly by ab initio calculations of molecular geometry [2, 3], as well as by correlations with experimental  $r_0$  or  $r_s$  values where these are well determined [3].

That the latter is not the case in MeCOX compounds is abundantly evident. In previous electron diffraction studies [4] it has been necessary to assume the presence of symmetrical methyl groups, and this is also the case with the microwave work [5-7] except for MeCOF, where Pierce and Krisher calculate structures for both symmetric and asymmetric methyl groups [8], and for MeCOCN. In the latter compound Pandey et al. find  $r_0CH_s > r_0CH_a$ , but  $r_sCH_s < r_sCH_a$  [9], while Zeil and Christen [10] calculate  $r_zCH_s = r_zCH_a$  from the data in [9].

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In such a situation, fresh data from IR studies of  $CHD_2$  substituted compounds are especially needed. A further interest in the present work is the possibility of finding the same variable *trans* effect of halogen that has been identified in alkanes [11] and alkenes [12]. Also, since the CN group was also to be studied, and little has been known up till now concerning the substituent effect of CN on CH stretching frequencies, it seemed worthwhile to include EtCN and so examine the  $\alpha$  and  $\beta$  effects of CN in the latter. For  $CH_3COOCH_3$ ,  $\nu_{CH}^{is}$  values were obtained in earlier work, for the methoxy group only [13].

An important advantage of the information derived from the study of  $CHD_2$  fundamental bands, as compared with that from high overtones of the unlabelled compounds [14], is the ability to relate the  $\nu_{CH}^{is}$  frequencies to those of the  $\nu_{as}CH_3$  and  $\nu_sCH_3$  motions, through the "3  $\times$  3" refinement of CH and CD stretching motions [15]. In particular, a difference in individual CH bond strength within the methyl group is always reflected in a splitting of  $\nu_{as}CH_3$ . Such splittings can be seen in earlier work on the acetyl halides, in both Raman and IR spectra [16—18] but two bands were assigned as separate fundamentals only in the case of  $CH_3COF$  [18].

In any kind of normal coordinate treatment, the frequency intervals between the  $\nu_{CH}^{is}$  values and the  $\nu_{as}$  CH<sub>3</sub> ones are primarily a function of two kinds of parameter: the stretch—stretch interaction constants  $f'_{aa}$ ,  $f'_{as}$  and the interbond angles  $H_aCH_a$ ,  $H_aCH_s$ , for the case of a methyl group with a plane of symmetry. The interaction constants  $f'_{aa}$  and  $f'_{as}$  as obtained by the  $3 \times 3$ refinement normally lie in the range 0.02-0.04 mdyn Å<sup>-1</sup>. In our past work we have assumed identical  $H_aCH_a$  and  $H_aCH_s$  angles in an unsymmetrical methyl group. With this assumption,  $f'_{aa}$  is sometimes found to be significantly different from  $f'_{as}$  [19]. Since for two of the present compounds, CH<sub>3</sub>COF and CH<sub>3</sub>COCN, there are indications that the  $H_aCH_a$  and  $H_aCH_s$  angles are significantly different, we explore below the possibility that variations in HCH angle may explain the variations in f' which otherwise appear.

## EXPERIMENTAL

The partially deuterated compounds  $CHD_2COX$  were prepared by the addition of ketene- $d_2$  to HX, where X was F, Cl, Br, I, OCD<sub>3</sub>, the ketene itself being prepared by the pyrolysis of  $(CD_3)_2CO$ . Samples of MeCOCN were prepared by reacting the appropriate acetyl bromide with CuCN [20].  $CHD_2$ - $CD_2CN$  was prepared by heating  $CHD_2CD_2Br$  with KCN overnight at 100° C in triethylene glycol which had previously been exchanged several times with  $D_2O$ .  $CD_3CHDCN$  was obtained as an impurity in  $CD_3CD_2CN$  by a similar reaction involving  $CD_3CD_2Br$  (Merck, Sharp, Dohme) in the same solvent, but incompletely exchanged\*. IR spectra were obtained from a Perkin Elmer 225 spectrometer calibrated to  $\pm 0.1$  cm<sup>-1</sup>. A few Raman spectra were

<sup>\*</sup>The undeuterated solvent gave pure CD<sub>3</sub>CH<sub>2</sub>CN.

recorded on a Cary 83 spectrometer with external recorder for frequency scale expansion, or on a Spex Ramalog instrument at the University of Glasgow.

## RESULTS

The IR bands are seen in Figs. 1-3 and the corresponding frequencies in Table 1.

# Assignments

Both  $CH_3$  and  $CHD_2$  spectra of acetyl fluoride show a pair of bands in the CH stretching region, the higher one an A/B type, the lower one, type C (Figs. 1 and 2). The presence of two weak  $CH_a$  and one strong  $CH_s$  bond is unmistakable. The type C band is much weaker in the chloride spectrum, only just visible in the bromide, and invisible in the iodide. The A/B type band moves downwards steadily in frequency from the fluoride to the iodide. However the C type one is essentially unchanged in the F, Cl and Br



Fig. 2. IR spectra in gas phase of CH<sub>3</sub>CXO compounds, 2975-3075 cm<sup>-1</sup>.





# TABLE 1

Molecule	Phase	vasCH3		vCHD,		
		a'	a"	CH <sub>s</sub>	CHa	
MeCOF	g	3042.5 m, A	3002.6 s, C	3025.4 m. A	2980.1 s. C	
MeCOCl	g	3026.9 m, A	3000,5 w, C	3004.0 m. A	2978.5 w.C	
MeCOBr	g	3021.6 m, A	2997.4 vvw. C	2994.9 m. A	2978.2 vw. C	
MeCOI	g	3013.3 m. A		2983.3 m. A	, ·-	
MeCOOMe	g	(3045 vw, max)	2993.7 vw. max	3012.0 w. A	2972.7 w.C	
MeCOCN	g	3027.5 w, A	2978.2 vw. C	3010 w. max	2957.5 w.C	
MeCOCN	ĩ	3022 w, bd, dp	2975 w, vbd, dp	3004.5 w, bd, dp	2951.7 m, p	
		$\nu_{as}CH_{3}/CH_{2}$	ν <sub>s</sub> , 2δCH <sub>2</sub>	vCHD₂/CHD		
MeCD,CN	g	2998.6 <sup>b</sup>		2973.7 s A		
CD <sub>3</sub> CH <sub>2</sub> CN	g	2966.5 s, C	2949.2 s, B 2869 m, B	2952 m, C		
			•			

Observed frequencies in MeCXO and EtCN<sup>a</sup>

<sup>a</sup>g = IR, gas phase; l = R, liquid. <sup>b</sup>Ref. 21.

compounds. It is reasonable therefore to predict that the iodide low frequency band lies close to the bromide one. Both of these effects are in keeping with the variable *trans* effect of halogens found in other types of compound, which alters the strength of the solitary in-plane CH bond, and with the constant gauche effect of halogen. In  $CHD_2COOCD_3$ , two bands, the higher A/B and the lower type C, are also clearly distinguishable (Fig. 1). The  $CH_3COOCD_3$  spectrum however is not only very weak (Fig. 2) but exhibits little detail in the contours. One maximum, at 2993 cm<sup>-1</sup>, fits well with an assignment as the  $a'' v_{as}$ CH<sub>3</sub> bond. In CHD<sub>2</sub>COCN, two bands are again seen (Fig. 1) of which the lower, at 2957.5 cm<sup>-1</sup> is unmistakably type C, but the higher with maximum at 3010 cm<sup>-1</sup> has an irregular contour. However, type A/B and C bands are clearly distinguishable in CH<sub>3</sub>COCN (Fig. 2). In the Raman spectrum of liquid CHD<sub>2</sub>COCN, two bands 3004.5 cm<sup>-1</sup> (weak) and 2951.7 cm<sup>-1</sup> (medium) are seen, whose intensities reflect the 1:2 distribution of strong and weak bonds deduced from the gas phase contours. Comparison of these liquid frequencies with those for CH<sub>3</sub>COCN in both gas and liquid phases leads us to prefer the value of 3010 cm<sup>-1</sup> for the  $\nu$ CH<sub>s</sub> band centre in the gas phase. The quantitative interrelation of these CHD<sub>2</sub> and CH<sub>3</sub> frequencies is discussed below.

In contrast to these results for acetyl compounds, is the spectrum of  $CHD_2CD_2CN$ , Fig. 3. This shows a single A type band at 2973.5 cm<sup>-1</sup>. The careful work of Heise [21] on the species  $CH_3CD_2CN$  places both a' and a"  $\nu_{as}CH_3$  bands at 2998.6 cm<sup>-1</sup> with no sign of splitting\*. We therefore infer that the three CH bonds are indistinguishable in strength. The spectrum of the  $CD_3CD_2CN$  sample has in the CH stretching region a prominent Q branch at 2952 cm<sup>-1</sup> which we assign to the  $CD_3CHDCN$  species:  $\nu_{as}CH_2$  of the  $CD_3CH_2CN$  species may just be distinguished at 2966.6 cm<sup>-1</sup> (Fig. 3). This assignment is readily checked by means of the approximate frequency sum rule for CH stretches. The spectrum of  $CD_3CH_2CN$  (Fig. 3) shows  $\nu_{as}CH_2$  (type C) and  $\nu_s$  (type B) at 2949 cm<sup>-1</sup> in resonance with  $2\delta CH_2$  at 2869 cm<sup>-1</sup>. Since  $\delta CH_2$  is found at 1445.6 cm<sup>-1</sup> [21] an allowance of 10 cm<sup>-1</sup> for a normal anharmonicity deficit on  $2\delta CH_2$  implies a Fermi resonance shift of 12 cm<sup>-1</sup> on  $\nu_s CH_2$ , placing  $\nu_s^0 CH_2$  at 2937 cm<sup>-1</sup>. The mean of  $\nu_{as} CH_2$  and  $\nu_s^0 CH_2$  is then 2952 cm<sup>-1</sup>, in agreement with the observed  $\nu CHD$  band.

## Discussion of results

Table 2 lists the  $\nu_{CH}^{is}$  values for all the MeCOX compounds so far studied together with the substituent effects  $S_t^X$  and  $S_g^X$ . The range of  $S_t^X$  values from fluoride to iodide (42 cm<sup>-1</sup>) is markedly larger than the corresponding one in ethyl halides (29 cm<sup>-1</sup>) but probably smaller than that in halogenated ethylenes [12]. The trans effects of CN and OMe are midway between those for F and Cl. The gauche effect of halogen is a constant increase, close to 34 cm<sup>-1</sup>, again rather larger than the similar effect in alkyl halides. Whereas the gauche effect of OMe is like that of a halogen, that of CN is markedly lower. The variation in the trans effect of halogen, as opposed to the constancy of the gauche one, results in a diminution of the asymmetry in bond strength from the fluoride to the iodide, where it is predicted to be negligible\*\*. While it is

<sup>\*</sup>The results of Wurrey et al. [22] are similar.

 $<sup>**\</sup>nu CH_aD_2$  is not actually observed.

#### **TABLE 2**

x	ν <sup>is</sup> CH <sub>s</sub>	ν <sup>is</sup> CH <sub>a</sub>	$S_{\mathrm{t}}^{\mathbf{X}}$	SgX
н	3002	2945		
Me	3004(4)	2946	2(5)	1
F	3025	2980	23	35
Cl	3004	2979	2	34
Br	2995	2978	7	33
I	2983	(2978)	-19	(33)
CN	3010	2958	8	່13
OMe	3012	2972	10	27

Isolated CH stretching frequencies and substituent effects in MeCXO<sup>a</sup>

 ${}^{a}S^{X} = \nu_{CH}^{is} (CH_{3}CXO) - \nu_{CH}^{is} (CH_{3}CHO); t = trans, g = gauche.$ 

tempting to interpret the relative weakness of the  $CH_a$  bond as due in some way to a hyperconjugative effect, the above influences of halogen suggest that more than one factor is operative. While chemists usually prefer to invoke electronic influences in discussing bond strength, perhaps the suggestion of Schegel et al. [23] that nuclear repulsions may play a dominant role in determining CH bond force constants should be considered more carefully in situations outside that in which their proposal was made, namely lone pair *trans* effects. This could include both the *trans* effects of halogen and methyl, the weakness of methyl  $CH_a$  bonds in methyl groups attached to C=C and C=O bonds, and the variation in strength of a CH bond rotating against a planar skeleton as in  $CH_3NO_2$  and  $CH_3BF_2$  [3].

Table 3 lists all known  $\nu_{CH}^{is}$  values for compounds containing CN, and their respective  $\alpha$  and  $\beta$  substituent effects. These appear to be in no way connected with the known effects of Me or halogen [3], and can only be described at present as irregular.

Table 4 shows the values of  $r_0$  predicted for all these compounds, together with such experimental values as are available. The largest differences in  $r_0$ CH within the same methyl group are predicted in acetaldehyde and acetone (0.006 Å), with acetyl cyanide (0.005<sub>s</sub>) and fluoride (0.005) close behind. Several of the microwave bond lengths agree with our predicted ones within their large experimental error. However the  $r_0$ ,  $r_s$  and  $r_z$  CH lengths in acetyl cyanide appear to us quite inaccurate\*.

In this connection it is of great interest that the difference  $\Delta r_e(CH_a - CH_s)$  calculated by an ab initio calculation in  $CH_3CONH_2$  [24] is 0.006 Å, a value coincident with what we predict here for similar compounds.

<sup>\*</sup>The inversion of the  $CH_a$ — $CH_s$  difference from  $r_o$  to  $r_s$  is discussed by Pandey et al. [9] in terms of four possible causes. Our present feeling is that their fourth cause, the assumption of equality of rCH and rCD, which they consider to be of negligible importance may be the principal reason for the anomalies here. The defects of  $r_s$  structures in symmetrical methyl groups have been analysed by Duncan [26].

Substituent effects for CN groups

Molecule	ν <sup>is</sup> CH	$S^{CN}_{lpha}$	Molecule	ν <sup>is</sup> CH	$S_t^{CN}$	$S_{g}^{CN}$
CH,	2992 <sup>a</sup>		CH <sub>1</sub> CH <sub>1</sub> CN (H <sub>e</sub> )	2974	24	
CH,CN	2985 <sup>a</sup>	—7	, (H <sub>a</sub> )	2974		24
$CH_{,}(CN),$	2963ª	-22	CH,COCN (H,)	3010	8	
сн,сн,	$2950^{a}$		(H <sub>a</sub> )	2958		13
CH, CH, CN	2952	2	· •			

<sup>a</sup>Ref. 3.

The differences in bond length within the methyl group should be accompanied by differences in dissociation energy, which may be calculated by the formula in [3]. In CH<sub>3</sub>CHO and (CH<sub>3</sub>)<sub>2</sub>CO, the CH<sub>a</sub> bond is weaker by 5 kcal mol<sup>-1</sup> than the CH<sub>s</sub> one.

A further effect which may be discerned in the CH stretching frequency data concerns the HCH inter bond angles in the methyl groups. Our data for MeCOF and MeCOCN when used in the  $3 \times 3$  refinement yield values of  $f'_{as}$ roughly twice those of  $f'_{aa}$ , if identical  $H_aCH_a$  and  $H_aCH_s$  angles are employed. Noticing that these two molecules were ones in which the microwave based  $H_aCH_s$  and  $H_aCH_a$  angles were markedly different, we found that use of these angles yielded  $f'_{as} \approx f'_{aa}$ . It was decided then to calculate  $H_aCH_s$  and  $H_aCH_a$  angles which would reproduce the frequency data, with  $f'_{as}$  and  $f'_{aa}$ both constrained to the value of 0.032 mdyn Å<sup>-1</sup>, a value which gives good agreement with observed angles for the fluoride. These angles are listed in Table 5. At this stage it can only be said that they look sensible, and that we may have a possible method for obtaining rough estimates of angular asymmetry in the methyl group.

There is of course no fundamental reason why  $f'_{as}$  should equal  $f'_{aa}$ . At the worst, these are only empirical parameters. However they have the same sign and similar order of magnitude to the harmonic stretch—stretch interaction constants calculated by ab initio methods [27] so that they may have genuine physical significance. If so, this would suggest that, since each f' is determined by a  $\nu_{as}CH_3-\nu CHD_2$  splitting, the anharmonicities of  $\nu_{as}CH_3$  and  $\nu CHD_2$  are similar, likewise the extent to which their frequencies involve contributions from bending or other lower lying motions in the whole molecule. Further study by ab initio calculations of both geometry and force constants of these molecules is clearly desirable.

## CONCLUSIONS

The methyl groups of CH<sub>3</sub>COX compounds, where X = H, Me, F, Cl, Br, CN, OMe all contain two weak and one strong CH bond. Those of CH<sub>3</sub>COI and CH<sub>3</sub>CH<sub>2</sub>CN are approximately equal in strength. The *trans* and *gauche* 

	r(obs)						r <sub>o</sub> (pred) <sup>a</sup>			
	Type	Ha		Hs	H <sub>a</sub> H <sub>s</sub>	Ref.	Ha		H <sub>s</sub>	H <sub>a</sub> – H <sub>s</sub>
CH <sub>3</sub> CHO	ŗ		1,086(5)		0(ass)	9	1.097 <sup>b</sup>	-	1,091 <sup>b</sup>	0.006
(CH <sub>1</sub> ), CO	۲. ۲		1.085(7)		0(ass)	7	1,097 <sup>b</sup>	-	1.091 <sup>b</sup>	0,006
CH, CFO	ד	1.096		1.082	0.014	80	1.093,		1.088,	0,005
			1.088(4)		0.0	4	•		•	
CH, CCIO	_ ۲		1.083(5)		0(ass)	ഹ	1.093,	-	1.091	0.002,
CH <sub>3</sub> CBrO	12 22		1.092(ass)		0(ass)	4	1,093,	-	1.092	0.001
CH <sub>3</sub> CIO	12 L		1.088(4)		0(ass)	4	(1.093,)		1.093	(0.000 <u>,</u> )
CH,COOMe <sup>c</sup>							1.094	-	1.090	0,004
CH, COCN	Ľ	1.067(3)		1,102(13)	-0.035	ი	1.095,		060.1	0,005,
	۲.	1.091(2)		1.083(4)	+0.009	6	L			•
	r2		1.083(7)		0.0	10				
CH, CH, CN	<u>ب</u>	1.091(1)		1.079(18)	0.012	25	1.094	Г	1,094	0.0
CH, CH, CN			1.094(1)			25	-	1.096		
CH,CONH,	r a	1.0830 <sup>d</sup>		1,0771 <sup>d</sup>	0.006 <sup>d</sup>	24				
-	-					-				

<sup>a</sup>This work, except where otherwise stated. <sup>b</sup>Ref. 1. <sup>c</sup>For OCH, data, see ref. 13. <sup>d</sup>Ab initio value (4–21G).

58

Comparison of CH bond lengths in  $CH_3CXO$  and  $CH_3CH_2CN$  (A)

#### TABLE 5

Molecule	fs	fa	H <sub>a</sub> CH <sub>s</sub>		H <sub>a</sub> CH <sub>a</sub>	
			Pred <sup>a</sup>	Obs <sup>b</sup>	Pred <sup>a</sup>	Obs <sup>b</sup>
СН,СНО	4.937°	4.744°			107.0	
CH,COCH,	4.953 <sup>c</sup>	4.750°			106.0	
CH_CFO	5,006	4.856	109,9	110.85 <sup>d</sup>	107.5	107.27 <sup>d</sup>
CH,CCIO	4,934	4,853	110.8		107,1	
CH_CBrO	4,905	4.852	111.0		105.3	
CH,CIO	4.866	(4.85)	110.8			
CH.COCN	4.957	4.783	110.6	$111.1(2.1)^{e}$	106.9	$105.1(1.6)^{e}$
CH <sub>3</sub> COOMe	4.953	4.829			107.5	

Stretching force constants and HCH angles in CH<sub>3</sub>CXO compounds

<sup>a</sup>The HCH angles predicted are those for which  $f'_{aa} = f'_{as} = 0.032 \text{ mdyn } \text{Å}^{-1}$ . <sup>b</sup>Where unequal HCH angles have been identified. <sup>c</sup>Ref. 1. <sup>d</sup>Ref. 8,  $r_s$ . <sup>c</sup>Ref. 9,  $r_s$ .

effects of halogen in acetyl halides are similar in kind but larger than those in alkyl compounds. The  $\alpha$  and  $\beta$  effects of CN are irregular by comparison. Comparison of  $\nu_{as}CH_3$  and  $\nu CHD_2$  frequencies possibly gives an indication of marked differences between  $H_aCH_a$  and  $H_aCH_s$  angles. The microwave-based CH bond lengths are very inaccurate.

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60

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