Vibrational spectra of 1,1-dichloroethanes and β CH stretching interaction force constants

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Abstract—Infrared and Raman spectra are described and assignments are reported for CH₃CDCl₂ and CD₃CHCl₂, together with new i.r. data for CH₃CHCl₂ and CD₂HCHCl₂. Using previously obtained "isolated" CH stretching frequencies, the above data enable the trans and gauche stretch-stretch interaction force constants to be determined: $f'_{g} = \pm 0.011$, $f'_{1} = \mp 0.026$ mdyn/Å. Similar values, $f'_{g} = +0.016$, $f'_{1} = -0.029$, may be obtained from the earlier spectra of CHD₂CHD₂ due to Van Riet.

The relations between the fundamental deformation bands and their overtones and combinations are examined in order to estimate the accuracy of predictions of v_s (= v_3) for the CH₃ and CD₃ groups from the 4 × 4 refinement and frequency sum rule. The data can be interpreted so as to give good agreement on the values of v_s^0 of 2920 cm⁻¹ (CH₃) and 2115 cm⁻¹ (CD₃), provided that there are significance resonance shifts on both $2\delta_a$ and $2\delta'_s$ levels. That this is the case seems to be true for the CD₃ group, but is uncertain for the CH₃ one.

INTRODUCTION

The CH stretching frequencies of CHD₂CDCl₂ and CD₃CHCl₂, previously determined in [1], represent "isolated" one in that they are free from coupling to other CH stretching frequencies and also from Fermi resonances such as occur in CH₃ and CD₃ groups. Shifts from these values to those found in CHD₂CHCl₂ should therefore reflect the vicinal CH–CH coupling, and yield information on the two stretch-stretch interaction constants: f'_{θ} , involving the *gauche* pair of CH bonds (atoms H₄ and H_{1,2}), and f'_{b} the *trans* CH bonds in which lie atoms H₄ and H₃.

The same force constants should determine the shifts in the CH and CH_3 stretching vibrations passing from CD_3CHCl_2 and CH_3CDCl_2 to CH_3CHCl_2 .

Since the shifts involved never exceed more than a few cm^{-1} and are often much smaller, the feasibility

of determining the interaction force constants depends critically on the validity of the assumption of "isolation". If a consistent set of constants can be determined, therefore, support for this assumption will have been obtained.

A by-product of the refinement calculations is the prediction of unperturbed values of $v_s(CH_3)$ and $v_s(CD_3)^*$ [2, 3]. In the previous study of chloroal-kanes [1], the predicted values of v_s^o have seemed to be too low, judging by the intensities found for $2\delta_a$ and $2\delta_s$ overtone bands. Perhaps a more reliable method of assessing Fermi resonance shifts is through the *frequencies* of the overtone bands, using estimates



^{*} The prediction of $v_{s}^{o}(CH_{3})$ can also be made more directly through the approximate frequency sum rule: $\Sigma_{3} v_{i}(CHD_{2}) = \Sigma_{3} v_{i}(CH_{3})$, which can be applied if two of the three $v(CH_{3})$ frequencies are known and unperturbed.

Assignments

of "normal" anharmonicity shifts of about 15 cm^{-1} for $2\delta_a(CH_3)$ and 10 cm^{-1} for $2\delta_a(CH_3)$ respectively [4]. We attempt such a study here.

Previous assignment studies have been made for the species CH_3CHCl_2 and CD_3CDCl_2 by DURIG et al. [5], following earlier work on the former by DAASCH et al [6]. Reference [7] also reviews conflicting studies on the location of the torsional mode. For our own work it is only necessary to recall that a" modes give rise to i.r. bands with type A contours, a' ones to type B/C [5].

EXPERIMENTAL

The CH₃CDCl₂ was prepared by reduction of CH₃CCl₃ by LiAlD₄ [8], the CD₃CHCl₂ by reacting CD₃CHO, prepared according to [9], with PCl₅. Both samples contained a small amount of the isotopic impurities (<5%), as identified by NMR, the former a small amount of the normal species and the latter a little CHD₂CHCl₂, which was the only source of information about this species. Infrared spectra in the vapour phase were recorded on two Perkin– Elmer 225 spectrometers, important bands being calibrated specially; the maxima of narrow Q branches are good to $\pm 0.1 \text{ cm}^{-1}$. Raman spectra in the gas phase in selected regions were obtained at the University of Bradford on a Spex 1401 spectrometer. Liquid phase Raman studies were made either on a Cary 83 instrument (calibration error $\pm 3 \text{ cm}^{-1}$) or on a Spex Ramanlog 4 spectrometer at the University of Glasgow (calibration error $\pm 1-2 \text{ cm}^{-1}$).

RESULTS

A set of assignments, complete except for the torsional frequency, together with the description of the frequencies, is given in Table 1.

Below 1500 cm⁻¹. There are few problems. Fig. 2 shows the i.r. CH₃ and CD₃ deformation bands. δ_a (CH₃) and (CD₃) should produce type A bands. The Q branch of the former is evident at 1451.8 cm⁻¹, while the centre of the later cannot be far from the minimum at 1057 cm⁻¹. The $\delta_a - \delta'_s$ splitting is therefore in both cases slight.

In CH₃CDCl₂ two bands are seen with Q branches at 1081.4 and 1085.4 cm⁻¹ (Fig. 3) which are assigned

Table 1. Fundamental vibration frequencies in 1,1-dichloroethanes

· · · · · · ·	CH ₃ CHCl ₂ ^{a,b}	CH ₁ CD(CD ₃ CHCl,*	24		
Α′	i.r. (gas)	i.r. (gas)	R (liq.)	i.r. (gas)	R (liq.)		
v(CH)	3015.6 m,C	2258.5 m,C		3006.3 m,C			
$v_1(CH_3)$	2996(est) ^c	3005.9 s,C		2253.0 ms,C			
$v_3(CH_3)$	2916(est) ^d	2916 (est) ^d		2118 ^d (est)			
$\delta'_{s}(CH_{3})$	1448.6 ms,C	1446.1 ms,C		1048.7 ms,C	1046 bd,w,dp		
$\delta_{s}(CH_{3})$	1383.8 ms,B/C	1383.9 m,B/C		1138.6 ms,B	1135 vw,pol		
δ(CH)	1284.2 ms,B	825 w,B	826 vw,dp	1267.0 ms,B	1265 w,pol		
$\rho(CH_3)$	1087 w	1118.8 m,B/C	1112 w,pol	864 w,B	859 m,pol		
v(CC)	983.5 ms,B	1081.4 s	1076 vw,pol?	955.5 w,B/C	956 vw,pol		
$v_{1}(CCl_{2})$	650.5 m,B	641.5 m,B	632 vs,pol	604 m,B	599 vs.pol		
$\delta(\mathbf{sk})^e$	404.5 w,B	399.5	402 m,pol	376 w,B	375 m,pol		
$\delta(CCl_2)$	273.5	272.0	274 m,pol	~ 269 vw,min	274 m,pol		
$\pi_{\rm H}/\pi_{\rm D}$ obs		1.8993		4.7633			
$\pi_{\rm H}/\pi_{\rm D}$ calc		$1.9463 \Delta^{2.5/6}$		5.0119 $\Delta = 5.2/_{0}$			
Α″							
$v_2(CH_3)$	2996.3 m,A	2996.3 m,A		2248.5 m,A			
$\delta_a(CH_3)$	~ 1450 w	1451.8 w		~1057			
δ(CH)	1230.4 s,A	885.2 ms,A	885 vw,dp	1230 s,A	1231 vw,dp		
$\rho(CH_3)$	1060.0 s,A	1085.4 s	1080 vw,dp	899.5 vs,A	890 bd,w,dp		
$v_a(CCl_2)$	707.7 s,A	696.8 s	681 w,dp	660.2 vs,A	644 m,bd,dp		
δ(sk)	317.0	315.5	319 w,dp	275 w,max	280 sh,dp		
t(CH ₃)	274 ^r	274 ^r		196 ^g (est)			
$\pi_{\rm H}/\pi_{\rm D}$ obs		1.3835^{h} $A = 0.8^{\circ}$		2.6804^{h} = 3.0%			
$\pi_{\rm H}/\pi_{\rm D}$ calc		1.3953 ^h / ^L = 0.0%		2.7001^{b}			

* This work.

^b These frequencies agree with those of ref. (5), within 3 cm^{-1} .

^c Calculated by 4×4 refinement to coincide with $v_2(CH_3)$ (a").

^d Estimated from 4×4 refinement.

 $\delta sk = skeletal bending.$

^f From ref. (5). Its value in CH₃CDCl₂ is calculated to be unchanged.

*Ratio t(CH₃)/t(CD₃) = 1.3952 calculated from formula 12-48 in C. H. Townes and A. L. Schawlow, *Microwave Spectroscopy*, McGraw-Hill, New York 1955, p. 328.

^h Ratios excluding torsion.



Fig. 2. Infrared bands due to δ (CH₃) and δ (CD₃) in CH₃CDCl₂ (1) and CD₃CHCl₂ (2) (gas phase).* Impurity.

to v(CC) (a') and $\rho(CH_3)$ (a'') respectively. While it is hard to decide which of the two bands is type A, and which type C, the above assignment is favoured very slightly by the product rule calculations.



Fig. 3. Infrared spectrum of CH₃CDCl₂ in the 1100-1060 cm⁻¹ range (gas phase).

Whereas in CH₃CDCl₂, δ (CCl₂) at 272 cm⁻¹ and δ_{sk} (a'') at 315.5 cm⁻¹ are readily distinguished, in CD₃CHCl₂ they overlap, forming in the i.r. spectrum a band of curious shape. In the Raman spectrum however, the presence of two frequencies, a higher depolarized shoulder and a lower, polarized, line, is plain to be seen. In the liquid phase Raman spectra recorded on the Spex Ramalog 4, no band was seen below 274 cm^{-1} in any sample. However, from the samples of CH₃CDCl₂ and CH₃CHCl₂, the Cary 83 instrument produced a weak band at 221 cm⁻¹ in the liquid in both cases, in agreement with the line reported by ALLEN et al. [7]. In view of the evidence of [5] that the torsional frequency is probably above 250 cm^{-1} , the origin of the 221 cm^{-1} line must remain in doubt.

v(CD) region: location of $v_s^o(CD)_3$). Figure 4 shows the i.r. and Raman spectra of CD₃CHCl₂ in this region, in the gas phase, while Table 2 includes the frequencies obtained both here and in the v(CH) region. vis values are also given, for convenience. We note that v(CD) is seen in CH₃CDCl₂ at 2258.5 cm⁻¹ and that $v'_{a}(CD_{3})$ and $v_{a}(CD_{3})$ occur in $CD_{3}CHCl_{2}$ at 2253.0 and 2248.5 cm⁻¹. The first of these would be expected near 2235 cm^{-1} , either on empirical grounds or from the 4×4 refinement, and it seems likely that a Fermi resonance is present here. We therefore agree with DURIG et al. s calculated assignment, in contrast with their observed frequency one. It was a surprise to find the main i.r. and Raman bands arising from $2\delta_a$ or $2\delta'_s$ modes differing in frequency by 15 cm^{-1} . Since it is well outside the



Fig. 4. Infrared and Raman spectra of CD₃CHCl₂ in the v(CD) region (gas phase).

expected calibration error, we attribute the Raman frequency at 2075.5 cm⁻¹ (which corresponds to an i.r. shoulder) to 2×1048.7 (δ'_s) and the i.r. one at 2090 cm⁻¹ to 2×1057 (δ_a).

The observed-calculated discrepancies are then 22 and 24 cm^{-1} respectively, suggesting Fermi resonance shifts of about 15 cm^{-1} and 17 cm^{-1} on the two bands^{*}. This result is surprising in that in the limit of complete degeneracy of δ_a and δ'_s , two bands will

* We allow 7 cm^{-1} and 10 cm^{-1} for normal anharmonicity in $\delta_a(\text{CD}_3)$ and $\delta_s(\text{CD}_3)$ modes respectively. appear for $2\delta_a$ corresponding to the *E* and *A* levels of a C_{3V} CH₃X molecule, only one of which can be in resonance with v_s . However there is no other obvious *a'* combination to account for the Raman frequency. The assignment of $\delta_s + \delta'_s$ at 2182.5 cm⁻¹ (*R*) yields an observed-calculated discrepancy of 5 cm⁻¹, which suggests little or no resonance. The i.r. band at 2191 cm⁻¹ (*A* type) would appear to be $\delta_s + \delta_a$, expected at 2195.6 cm⁻¹, which would confirm our assignment of the centre of the δ_a band. Finally, although $2\delta_s$ at 2279 (i.r.) is very weak in the i.r., it is a medium band in the Raman spectrum

Table 2. Observed vibrational frequencies and assignments in v(CH) and v(CD) regions of 1,1-dichloroethanes

	CH ₃ CHCl ₂	CH ₃ CD	Cl,	CD ₃ CHCl ₂	
	i.r. (gas)	i.r. (gas)	R (gas)	i.r. (gas)	R (gas)
v(CH)	3015.6(1)s,C	2258.5(1)m,C		3006.3(1)s,C	
vi(CH _a)		3005.9(1)s.C		2253.0(3)ms,C	2254 m
v.(CHJ)	2996.3(1)s.A	2996.3(1)s.A		2248.5(3)ms,A	~ 2248 sh
V.(CH ₂)	2946.4(2)m.B	2945.2(2)m.B		2131(1)m,B	2134 vs
2δ.			?2883 sh	2090(1)w,B	
2δ'.	2877.1(2)w.B	2872.4(2)w,B	2876		2075.5 m
$\delta_1 + \delta_2$	()	2831.6(1)vw.A		?2191(2)vw.A	
$\delta' + \sigma$.	2826.9(1)vw,C	2825.1(1)vw,C		~ 2175 sh	2182.5 vw
2δ,	2747.5(10)vw,B	2748.0(5)vw,B		2279(2)vw,Q	2276 m,bd
	CHD ₂ CDCl ₂		CHD ₂ CHCl ₂		
CUH	(I.r. gas)		(1.1. gas)		
VCH"	2983.7(1)		2980.93(3)		
VCH	2971.3(1)		29/1.1(1)		

Error in last figure quoted in parentheses.

	Vobs						
Mode	Vcalc	i.r. R		$v_{calc} - v_{obs}$	$\Delta v_{\rm FR}$		
$\overline{\delta'_s}$		1048.7					
δ_a		1057					
δ,		1138.6					
$2\delta'_{s}$	2097.4		2075.5	22	15		
$\delta_a + \delta'_s$	2105.7						
$2\delta_a$	2114	2090		24	17		
$\delta_s + \delta'_s$	2187.3	~ 2175 sh	2182.5	5			
$\delta_s + \delta_a$	2195.6	2191		4.6			
2δ ,	2277.2	2279	2276	2	-12		
•				total	+20		
v,		2131	2134				
v_*^o	2111						
v_s^o (4 × 4)	2118						

Table 3. Position of $v_{4}^{0}(CD_{3})$ in CD₃CHCl₂

(Fig. 4) and since it would have been expected near 2267 cm⁻¹, it appears to have been displaced upwards by about 12 cm⁻¹. These assignments are summarized in Table 3, together with the conclusion that the strongest band at 2131 cm⁻¹ (i.r.)—2134 cm⁻¹ (R)—is v_s displaced upwards from an unperturbed value of 2111 cm⁻¹. The 4 × 4 refinement below in fact predicts v_s^o at 2118 cm⁻¹. The agreement is satisfactory, considering the assumptions involved.

CH stretching region. $\delta_s(CH_3)$ in CH₃CDCl₂ now being well below $\delta_a(CH_3)$, $2\delta_s(CH_3)$ is displaced downwards. The Fermi resonance shift involved is therefore 5 cm^{-1} (Table 4). The combination bands $\delta_s + \delta_a$ and $\delta_s + \delta'_s$ are both seen in the i.r. (Fig. 5) at 2831.6 cm⁻¹ (type A) and 2825.1 (type C), with observed-calculated discrepancies of 4 and 5 cm⁻¹ respectively. These bands therefore confirm the centre chosen for $\delta_a(CH_3)$ (Fig. 2). The assignment of the $2\delta_a$ and $2\delta'_s$ bands however presents difficulties. The main i.r. band at

2872.4 would appear to be 2×1446.1 , $2\delta'_s$, with a resonance shift of 10 cm^{-1} . The band is rather broad to higher frequency. In the Raman spectrum the main band lies at 2876 cm⁻¹, which may just lie within calibration error of the i.r. frequency. It carries a shoulder however at 2883 cm⁻¹. If the latter is $2\delta_a$, expected at 2903.6 cm⁻¹, a Fermi resonance shift of about $11-10 \,\mathrm{cm}^{-1}$ has occurred. v_s , observed at 2945.2 cm^{-1} , may therefore have been displaced by up to 25 cm^{-1} so that v_s^o may lie as low as 2920 cm^{-1} . This lies roughly half way between the values predicted by the frequency sum (2924 cm^{-1}) and the refinement (2916 cm⁻¹). We feel uneasy about this analysis however, in view of the close proximity of the 2883 and 2876 cm⁻¹ frequencies and of the theoretical point made above in connection with $v_s(CD_3)$. It is possible that $2\delta_a$ has not been seen at all, that the high frequency shoulders seen in both the i.r. and the Raman are merely the result of the strong

Mode	v_{calc}	IR	v _{obs} R	$v_{calc} - v_{obs}$	$\Delta v_{\rm FR}$
δ.	i dan sekara karangan se	1383.9		·	
δ'.		1446.1			
δ_{a}		1451.8			
2δ.	2767.8	2748.0		19.8	5
$\delta_{\bullet} + \delta'_{\bullet}$	2830	2825.1		4.9	
$\delta_1 + \delta_2$	2835.7	2831.6		4.1	
28'	2892.2	2872.4	2876	19.8	10
$2\delta_{a}$	2903.6		?2883	20.6	211
$\delta_a + \delta'_{\bullet}$	2897.9				
• •				total	226
v.		2945.2			
v.(anh)	?2919				
$v_{\bullet}^{o}(\Sigma v)$	2924				
$v_s^o(4 \times 4)$	2916				

Table 4. Position of v_e(CH₃) in CH₃CDCl₂



Fig. 5. Infrared spectra of CH_3CDCl_2 and CD_3CHCl_2 , in gas phase, in the range 3050-2800 cm⁻¹. (o.e): ordinate expansion.

Coriolis effects that must set in just before the degeneracy becomes complete. In this case, only 10 cm^{-1} resonance shift may be gleaned from this band, and v_s^o would then be expected at 2930 cm⁻¹.

Considering now the higher fundamentals, we note that the prediction of an a' fundamental at 2996 cm⁻¹ in CH₃CHCl₂[1] is confirmed by its position at 3005.9 cm⁻¹ in CH₃CDCl₂. Mixing of the v(CH) and v'₃(CH₃) modes in CH₃CHCl₂ is in fact almost complete. Figure 5 shows also the CH stretching region of CD₃CHCl₂. The impurity bands due to CHD₂CHCl₂ are comparatively weak.

For the product rule checks, moments of inertia were calculated for a possible geometry: $\alpha_{\rm HCH}^{a\nu} = 109.0^{\circ}$, $r_{\rm CH} = 1.093$ Å, $r_{\rm CC1} = 1.80$ Å and other angles tetrahedral. Values of $\nu_{s}^{o}(\rm CH_{3})$ and (CD₃) were taken from the 4 × 4 refinement below, and in the a'' species, the contribution from the torsional mode was calculated and removed before comparison with the observed product ratios. The observed–calculated discrepancies seem reasonable in view of the numbers of degrees of freedom of motion of the atoms substituted. They are of course rather sensitive to the accuracy of the frequencies below 400 cm^{-1} . Correspondance with the similar discrepancies found for CD₃CDCl₂ in [5] is fair, only our value for the *a'* species of CH₃CDCl₂ appearing a little high.

Force constant calculations

It was found feasible to refine both the methyl group force constants (2 diagonal, 2 off-diagonal) and the remaining ones in one 4×4 refinement (Table 5). The methyl force constants are determined by the isolated CH stretching frequencies and by v_a and v'_a for the CH₃ group in CH₃CDCl₂. The two geminal interaction constants differ but slightly from each other for this molecule. The vicinal interaction force constants f'_{θ} and f'_{t} are determined partly by the coupling shift in v_{CH} from CD_3CHCl_2 to CH₃CHCl₂*, but more directly by the Δv_{CH}^{H} and Δv_{CH}^{Cl} shifts of -2.75 and -0.2 cm^{-1} respectively, from their isolated values to those in CHD₂CHCl₂. It is at once clear that f'_t is rather larger than f'_a [†]. The three shifts are well fitted by the following values of the two parameters:

$$f'_{g} = \pm 0.011_{4}$$
 $f'_{t} = \mp 0.026_{5}$.

The opposite signs of f'_{g} and f'_{t} result from the magnitude of the coupling $v_{CH} - v'_{s}$ in CH₃CHCl₂ which depends essentially on $|2f'_{g} - f'_{t}|$. It is interesting to note that the coupling $v_{CH} - v_{s}$ which depends roughly on $|2f'_{g} + f'_{t}|$ is zero. Since δ'_{s} rises by 2.5 cm⁻¹ from CH₃CDCl₂ to CH₃CHCl₂, $2\delta'_{s}$ should rise by 5.0 cm⁻¹ and is in fact seen to rise by 4.7 cm⁻¹

^{*} Among the possible shifts from the species CH_3CDCl_2 to CH_3CHCl_2 , $v'_a(CH_3)$ is not observed in the latter, $v_a(CH_3)$ cannot move, being in the *a*" symmetry class, and $v_a(CH_3)$ is initially suspect due to possible Fermi resonances.

 $[\]dagger$ The sensitivity of f' to a shift increases as the shift diminishes: the value of f' for such a shift is therefore less well-defined.

		v _{obs}	σ_v^*	Vcalc	E	$\Delta v_{ m obs}$ †	$\Delta v_{\rm calc}^{\dagger}$
Н3-Н	a'	3015.6	0.2	3015.55	+0.05	9.3	9.25
-	a'	un.		2996.49			-9.41
	a"	2996.3	2	2996.3	0		
	a'	un.		2916.03			0
H3-D	a'	3005.9	0.1	3005.9	0		
	a"	2996.3	0.1	2996.3	0		
	a'	un.		2916.03			
	a'	2258.5	1000	2231.5	+27.0		
D ₃ -H	a'	3006.3	0.1	3006.3			
•	a'	2253.0	10	2253.0	0		
	a"	2248.5	10	2246.1	+ 2.4		
	a'	un.		2118.2			
D₃–H	a'	3006.3	0.1	3006.3			
	a'	2253.0	10	2253.0	0		
	<i>a</i> ″	2248.5	10	2246.1	+ 2.4		
	a'	un.		2118.2			
D ₃ –D	a'	un.		2255.2			
-	<i>a</i> ″	un.		2246.1			
	a'	un.		2229.1			
	a'	un.		2218.2			
HDD-D		2971.3	0.1	2971.34	-0.04		
DDH-D	a'	2983.7	0.1	2983.71	-0.01		
HDD-H		(3006.0)	10	3006.7			
		2971.1	0.2	2970.94	+0.16	-0.2	-0.40
DDH-H	a'	(3006.0)	10	3009.9			
		2980.95	0.2	2980.89	+ 0.06	- 2.75	- 2.82
***			F	matrix			
r ₁	4.82	92	0.025	3	0.0232		0.0114
r ₂			4.829	2	0.0232		0.0114
гз					4.8693	_	0.0265
r ₄							4.9503
			$f'_{g} = 0.0$	114 ± 0.00	08		

Table 5. 4×4 refinement of CH and CD stretching frequencies

Notes: $\alpha_{HCH} = 107.8^{\circ}$, un. = unknown; v(CD) is divided by F = 1.011 before input, output remultiplied by F.

* σ_v is artificially small in many cases so that due weight can be applied to the *shifts*. For this reason errors elsewhere in the F matrix are not quoted.

[†] Coupling shifts either from CH₃CDCl₂ and CD₃CHCl₂ to CH₃CHCl₂ or from CHD₂CDCl₂ to CHD₂CHCl₂.

 $(2872.4 \rightarrow 2877.1 \text{ cm}^{-1})$. The shift expected for v_s^o is therefore no greater than the 1 cm^{-1} one seen, $(2945.2 \rightarrow 2946.4 \text{ cm}^{-1})$ and possibly less, since δ_a may also rise. If f'_g and f'_t had had similar signs, the shift would have been appreciably greater. While there is no indication here of the absolute signs of f'_g and f'_t in these spectra,* the values found resemble closely those in the ethyl and isopropyl chloride, bromide and iodide, where evidence for f'_t being negative is present [10].

A similar difference between f'_t and f'_c (cis coupling) was found in 1,2-dichloro and 1,2-dibromoethylenes,

although in the second of those, the sign of f'_t and f'_{c} appear to be the same [11]. Another compound in which indications of vicinal coupling appear is CHD₂-CHD₂, studied by VAN RIET [12]. Here, v_{CH}^{is} (from the species CHD_2CD_3) is at 2950 cm⁻¹, and in CHD₂CHD₂ two Raman frequencies are found at 2955 and 2941 cm⁻¹, with various i.r. ones between 2947.8 and 2957.4 cm⁻¹. If we assign the 2941 cm⁻¹ frequency to the species with C_{2h} symmetry, in agreement with Van Riet, we find $f'_{t} = -0.029$, while the other Raman line at 2955 cm⁻¹, which is likely to represent the in-phase coupled CH stretching motion in the C₂ species, yields $f'_{g} = +0.016$. The out ofphase coupled motions should then be 2959 (C2h) and 2945 (C₂) respectively, and i.r. Q branches can certainly be found close to these values.

^{*} The absence of any coupling in the G matrix means that the observed frequencies are independent of the *absolute* signs of f'_g and f'_t , only on their *relative* ones.

Further evidence for vicinal coupling of an even higher extent is found in the i.r. spectra of the ethylene oxide species $(CHD_2)_2O$ [13] although here the geometrical relation of the CH bonds is different.

The above results for ethane are essentially confirmed by two recent *ab initio* calculations of force constants, [14, 15], which yield the following values for f'_{a} and f'_{t} ;

	PM [14]	BA [15]	this work
f'_t	-0.021	-0.017_{7}	-0.029
f'a	0.014	-0.015_{3}	-0.016

The difference between predicted and observed magnitudes is probably significant for f'_{t} .

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