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Infra-red spectra of ¹³CD₃GeH₃ and DFT studies of force constants and electrical properties in methylsilane and methylgermane¹

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Abstract

New infra-red data are reported for some fundamental bands of ¹³CD₃GeH₃ in the gas phase. Triple-5 DFT calculations of geometry and force field have been made for CH₄, SiH₄, GeH₄, CH₃SiH₃ and CH₃GeH₃. The DFT force fields for methylsilane and methylgermane are scaled (SDFT) on all available data, including harmonised frequencies and frequency shifts, Coriolis constants and centrifugal distortion coefficients. Comparison of scale factors reveals considerable variation. Empirical force fields (ESDFT) are determined, a number of off-diagonal constants being constrained to SDFT values. Problems remaining in the observed data are identified.

Atomic polar tensors from the DFT calculations are used to obtain King effective atomic charges χ and bond dipole derivatives $d\mu/dr$ with respect to terminal bond stretching. Comparison between silanes and germanes reveals common trends in bending and stretching dipole moments together with the inductive effect of a methyl group. © 1997 Elsevier Science B.V.

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1. Introduction

Analysis of the vibrational spectrum of a molecule is now normally accompanied by a quantum-mechanical calculation of its geometry and force field. Prediction by the latter means of infra-red and Raman intensities can also provide useful qualitative information for the interpretation of the spectra. While for small molecules sufficiently sophisticated quantum-mechanical (QM) treatments can be employed to reproduce fundamental and other frequencies to within about 10 cm⁻¹ without recourse to further adjustment, see [1] for C₂H₄, for most molecules high-accuracy methods are too expensive to be practicable. In general it is then necessary to use less rigorous methods whose force fields need to be scaled if a satisfactory description of the observed spectra is to be obtained. Procedures for such scaling have been developed by several workers [2–4], that of Pulay *et al.* [2] being the most commonly followed. Scale factors are associated with each diagonal force constant corresponding to a particular symmetry coordinate, while off-diagonal constants are scaled by the geometric mean of the factors for the two diagonal constants concerned. In general, the Pulay approach has been to adopt a limited number of scale factors. Thus for a hydrocarbon, these might include one each for CH and CC stretching and

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³ Dedicated to Professor Kozo Kuchitsu on the occasion of his 70th birthday.

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for CH and skeletal bending. Since the factors are normally determined by a least-squares fit to observed vibration frequencies, the extent to which they depart from unity necessarily stems both from the deficiencies of the particular level of QM calculation of harmonic frequency and also from the fact that the observed data will be affected by anharmonicity, to an extent which in many cases amounts to 1-4%, the higher limit applying to stretching vibrations of bonds involving hydrogen.

In a test of the QM calculation it is therefore preferable to remove the effects of anharmonicity as best one may. An additional reason for attempting this is that scaling of the QM force field on the basis of the frequencies of a single isotope only may not reveal differences in scale factors that may be present, because the necessary information is lacking to determine them. The introduction of isotopic substitution alters the composition of the normal coordinates which may help to show that more independently varying scale factors are needed. However, the presence of anharmonicity inevitably introduces an element of incompatibility between isotopic data, owing the varying effect that it has on the frequencies of the different species.

Where anharmonicity corrections have been applied, evidence has been obtained to show that as the level of treatment is raised, as in recent calculations for trimethyl phosphine [5] and trimethylamine [6], scale factors for different types of motion both converge on each other and also approach closer to unity, which is satisfying.

The lengths to which one decides to go are, of course, dependent on one's objective. For a rough understanding of the vibrational spectrum a small number of scale factors may be adequate. However, in many situations more precise predictions are needed, for example:

- 1. in deciding on the assignment of bands less than 20 cm⁻¹ apart;
- 2. in elucidating Fermi resonances;
- 3. in identifying ${}^{R}Q_{0}$ in perpendicular bands for which high-resolution measurements are unavailable and intensity variations amongst the *Q*-branches are inconspicuous;
- 4. in determining accurate normal coordinates. The latter will be needed if observed intensities are to

be interpreted. If any of the normal coordinates represent highly coupled motions, for whose individual symmetry force constants different scale factors are in principle likely to be required, then a primitive scaling exercise may yield a misleading composition.

In the same situation, another pitfall may be experienced. The scaling procedure which alters each off-diagonal force constant by the geometric mean of the scale factors applicable to the diagonal ones cannot handle a situation where a small QM offdiagonal constant may be in error by 50% or more. Instances of this nature have recently been identified in a number of molecules where sufficient frequency data were available to define very many scale factors [7-10]. It needs to be said that wherever potential energy distributions are quoted that have been derived from SQM force fields with only limited attention to scaling by the Pulay method, substantial errors may be expected where the vibrations concerned involve coupling between the symmetry coordinates concerned.

For an investigation of this kind, experience suggests that the level of treatment is not of primary importance. Density functional theory (DFT) has become increasingly popular as an economical way of introducing electron correlation and many molecules have been so treated, including several extensive surveys [11,12] and especially [13]. In general, vibration frequencies tend to be calculated too low by this approach, in contrast to *ab initio* methods which yield ones higher than those observed, with or without corrections for anharmonicity. DFT-based scale factors are therefore typically greater than unity in cases where anharmonic corrections have been applied to the data.

Molecules suitable for subjecting a QM approach to a close scrutiny should be those for which as many kinds of data as possible are available, particularly those which reflect directly the normal coordinates involved, such as heavy isotope frequency shifts and Coriolis constants. Preferably also there should be atoms from several rows of the Periodic Table present. Methylsilane and methylgermane fall nicely into this category.

Data for methylsilane species have been reviewed recently [14] and force fields for methylsilane calculated [15], the latter including both a scaled ab initio force field (SAIFF) based on a double- ζab initio treatment and also an empirical one with SAI constraints (ESAIFF). Unfortunately a transcription error in the input file for this calculation introduced some error into the calculation of centrifugal distortion constants, rendering a repetition desirable.

In the case of methylgermane, two prior infra-red studies [16,17] leave doubts about certain band centres and do not report data for any ¹³C species. The fatter are the main probe of normal coordinate composition in the A_1 species, the *E* species benefitting in addition from the Coriolis coefficient data. We have partly remedied this deficiency by recording infra-red spectra from the species ¹³CD₃GeH₃.

A limited scaling exercise has been carried out recently on CH₃SiH₃ and CH₃GeH₃ by using frequency data only for just the parent species [18]. This was based on an SCF force field in which effective core potential wave functions were used for Si and Ge and standard 6-31G** functions on C and H. With just six scale factors (including one for the torsion) deviations between observed and calculated frequencies reached a maximum of 4.5%, which we find worrying. One interesting feature of this work is the variation in the scale factor for a particular kind of motion, e.g., MH (M = Si,Ge) stretching or bending from the MH₄ molecule to the CH₃MH₃ one. We wished to see if this could be established in a detailed scaling exercise at a higher level of treatment, with anharmonicity corrections applied to the frequency data. We have therefore calculated also SDFT force fields for CH₄, SiH₄ and GeH₄, using in these cases only frequency data since there are no normal coordinate problems in these molecules.

DFT geometries for all four compounds also provide the basis for a comparison of CH and MH bond length changes between CH_4 or MH_4 and the methyl compounds, with those predicted from the isolated stretching frequencies in these compounds [19–21].

A similar comparison between MH_4 and $MeMH_3$ compounds may be made in respect of the electrical properties involved. Atomic polar tensors, P_x for each atom, which consist of the dipole derivatives in three directions with respect to the three possible Cartesian displacements of the atom [22,23], are obtained in all

QM packages that have the capacity to predict infrared intensities, as the starting point for the intensity calculation. These tensors are characterised by a number of invariants, including the King effective atomic charge χ , given by the square root of the sum of the squares of all elements [24]

$$\chi^2 = \operatorname{Trace}\{(\mathbf{P}_x) \cdot (\mathbf{P}_x)'\}/3$$

the mean atomic dipole moment \overline{P} , which is the mean of the diagonal elements of the tensor, and the anisotropy β , given by [22]

$$\beta^2 = 4.5 \{ \chi^2 - \mathbf{P}^2 \}$$

The quantity \bar{P}/β has been used as a measure of the "charge undeformability" associated with the atom, i.e., the extent to which charge stays on the atom as it moves in various ways during the different vibrations [25].

If the axes with reference to which the polar tensor for a terminal atom in a bond has been calculated, are rotated so that one axis, e.g., the z one, lies along the bond direction, then the corresponding column elements yield the components of the dipole moment with respect to bond stretching, $d\mu/dr$, from which in turn the magnitude and direction of this vector can be obtained [22]. For the H atom in a tetrahedal MH₄ molecule, the resulting tensor will be diagonal, the *xx* and *yy* elements each equal to the bending bond moment divided by the bond length, while the *zz* element is itself $d\mu/dr$.

In cases of lower symmetry such as a C_{3v} -type molecule MH3 or CH3MH3, small off-diagonal elements in the z column show that $d\mu/dr$ for a CH or SiH bond lies off the bond direction to an extent which appears to depend on the polarisablity of the atom to which the CH₃ or MH₃ group is attached [26,27]. The maximum displacement noted so far occurs in CH₃I [26], where the off-bond angle is 62°. Where stretching of the bonds concerned contributes to almost 100% of the motion in the vibration, as is the case for CH₃, SiH₃ or GeH₃ groups, the angle which the $d\mu/dr$ vector makes with respect to the bond direction is the dominant factor in determining the distribution of infra-red intensity between bands due to the symmetric and antisymmetric stretching motions. In the case of SiH₃ and GeH₃ groups the bands due to these motions overlap wholly in the spectrum, and in the absence of high-resolution line

intensity measurements, there is no experimental means of dividing the observed inensity between the A_{\perp} and *E* bands concerned. Recourse has then to be made to QM predictions which, though liable to considerable absolute error, may yet give good indications of relative intensity. Elsewhere in the spectrum relative intensities will also require high-quality normal coordinates, but in the MH stretching region composition of the modes is not an issue and what matters is the angle which $d\mu/dr$ makes with respect to the bond.

This is of current interest in that infra-red intensity data for several species of methylsilane were obtained in the course of this work which will be discussed elsewhere [28].

2. Experimental: results and discussion of spectra

 13 CD₃GeH₃ was prepared by reacting 13 CD₃I (Merck, Sharp and Dohme, 98% D, 99% 13 C) with GeH₄ in a dimethyl sulfoxide/KOH slurry. Infra-red spectra in the gas phase were recorded on a Nicolet 7199 FTIR spectrometer at a resolution of 0.06 cm⁻¹.

2.1. Perpendicular bands

Q-branches for the individual ⁷⁰Ge, ⁷²Ge and ⁷⁴Ge isotopomers of ¹³CD₃GeH₃ were resolved only in the perpendicular band due to ν_8 . *Q*-branch maxima for the latter and also for the bands due to ν_7 , ν_9 , ν_{10} and ν_{12} are listed in Table 1, which includes also analyses in terms of an equation quadratic in *K*. Band centres ν_0 , inertial constants *A'* and Coriolis coefficients ζ were obtained by using the ground-state parameters of Table 2 (essentially those under structure I in Table 4 of [21]), and the assumptions B'' = B' and $(A\zeta)' = A'' \times \zeta$.

In his analyses of ${}^{12}\text{CD}_3\text{GeH}_3$ bands [17], Mackenzie appears to have used a slightly incorrect value of A". We have therefore reanalysed those ${}^{12}\text{CD}_3\text{GeH}_3$ bands for which Q-branch maxima were listed in [17], namely ν_7 , ν_9 , ν_{10} and ν_{12} , by using the ground-state constants in Table 2.²

Choice of ${}^{R}Q_{0}$ in these bands is difficult owing to the comparatively minor strong-weak-weak intensity variation in *Q*-branch intensity with value of *K*, not helped by the spread of Ge isotopic absorption. Influenced largely by a comparison of the matrix data of Oxton [29] for both methylgermane and methylsilane with the gas phase results, led us to alternative assignments of the Q-branches in ν_{10} and ν_{12} of ${}^{12}CD_3$ and with the aid of initial estimates of $^{13-12}$ C frequency shifts to the assignments for ν_{10} and v_{12} for ¹³CD₃GeH₃ found in Table 1. Several arguments suggested to us that ν_{10} for CH₃GeH₃ also needed to be reassigned from [16] or [17]. Firstly, in methylsilane this mode falls from gas to matrix by about 7.3 cm⁻¹ and a similar fall might be expected in methylgermane. With the former assignment v_{10} rises by 2.1 cm⁻¹ from gas to matrix. Secondly, the scaled DFT force field predicts a downwards displacement in ν_{10} of about 8 cm⁻¹ from the ¹²CH₃ species to the ¹²CD₃ one. For this reason we have moved ${}^{R}Q_{0}$ up three O-branches, assuming the strong-weak-weak intensity alternation to be observable (the original spectra were no longer available). The gas - matrix shift then becomes 9.3 cm^{-1} .

 ν_{10} for ¹²CD₃GeH₃ represents a greater problem. The matrix value [29] of 892.0 cm⁻¹ suggests that the band centre in the gas phase should be near 900 cm⁻¹, instead of 892.9 cm⁻¹ [17]. Here it must be close to the overtone level $2\nu_{12}$, since ν_{12} is at 450.32 cm⁻¹ and a Fermi resonance with the *E* component must be expected.³

Evidence for such a resonance comes from the ζ value, which for any assignment of ν_{10} has to be around -0.30, where the SDFT force field requires -0.24^4 , and from the ¹²⁻¹³C shift of 0.68 cm⁻¹ which is calculated to be 0.08 cm⁻¹ by the SDFTFF. The shift expected on $2\nu_{12}$ is 0.76 cm⁻¹.

However, there is no indication in the account of the matrix spectra for an additional peak in this region [29]. Our choice of ${}^{R}Q_{0}$ at 906.70 cm⁻¹, in agreement with Griffiths [16], assumes a modest amount of resonance. Clearly a high-resolution study of mono-isotopic species of 12 CD₃GeH₃ will be needed to clarify this region of the spectrum. No weight was given to any data for ν_{10} in CD₃GeH₃ species in the later calculations.

 $^{^{2}}$ A quadratic fit was also employed here. It is not stated what was used in [17].

¹ The same resonance in ¹²CH₃GeH₃ should be negligible since $2\nu_{12}$ should occur near 1000 cm⁻¹.

⁴ We are unable to reproduce the ζ_{10} value of -0.2735 quoted in [17].

Table 1 *Q*-branch maxima (cm⁻¹) and analyses for *E* species bands in 13 CD₃GeH₃.

K	ν ₇ (72.59)	ν ₈ (70)	$\nu_{8}(72)$	$\nu_8(74)$	v ₉ (72.59)	ν ₁₀ (72.59)	$\nu_{12}(72.59)$
	3000 +	2000 +	2000 +	2000 +	1000 +		
17	58.476			124.197			
16	56.708			121.952			
15	54.952			119.697		953.973	475.970
14	53.194	118.115		117.369		950.608	474.218
13	51.416	115.909	115.505	115.124		947.267	472,429
12	49.682	113.609	113.282	112.889	75.921	944.022	470.716
11	48.066	111.398	110.995	110.607	72.801	940.716	468.990
10	46.310	109.160	108.746	108.372	69.642	937.496	467.257
9	44.551	106.908	106.485	106.099	66.400	934.270	465.560
8	42.762	104.655	104.216	103.817	63.208	931.083	463.870
7	40.984	102.331	101.929	101.532	60.001	927.918	462.156
6	39.191	99.969	99.652	99.2.37	56.812	924.764	460,460
5	37.402	97.678	97,335	96.928	53.599	921.607	458.766
4	35.608	95.385	94.928	94.612	50.403	918.489	457.115
3	33.806	93.067	92.616	92.287	47.196	915.402	455.430
2	32.000	90.747	90.294	89.845			453.750
1	30.181	88.458	88.041		40,740	909.247	452.127
0	28.354	86.077	85.610	85.190	37,583	906.067	450.477
-1	26.548	83.725	83.275	82.850	34,390	903.152	448.814
-2	24.736				31.225	900.103	447.218
-3	22.934	78.911	78.467	78,030	28.036	897.114	
-4	21.089	76.612	76.162	75.739	24.893	894.122	443.941
-5	19.258	74.178	73.722	73.287	21.677	891.090	442.357
-6	17.412				18.526	888.025	440,756
-7	15.635	69.296	68.840	68,390	15,306	885.018	439,169
-8	13.824	66.920	66.452	66.007		882,000	437,602
-9		64.509	64.034	63.578		879,000	436,004
-10		62.091	61.609	61.155			434,462
-11		59.656	59.171	58.717			432.887
-12		57.217	56.727	56.272			431.361
-13		54.771	54.280	53.806			429.889
-14		52.325	51.814	51.337			428.283
-15		49.851	49.345	48.867			426.778
-16		47.384	46.874	46.393			425.300
-17		44.912	44.401				423.739
-18			41.958				
α (cm ⁻¹) a	2228.398(12)	2086.045(11)	2085.602(11)	2085.185(11)	1037.614(13)	906.132(24)	450.464(6)
β (cm ⁻¹) ⁻¹	1.8105(20)	2.3515(8)	2.3562(9)	2.3608(7)	3.1910(20)	3.0662(31)	1.6399(4)
$10^{3}\gamma$ (cm $^{3})^{a}$	-2.57(18)	-4.16(9)	-4.04(9)	-4.08(8)	6.84(28)	7.60(36)	4.04(5)
σ (cm ⁻¹)	0.046	0.037	0.039	0,039	0.036	0.080	0.021
$v_{\rm u} ({\rm cm}^{-1})$	2227.70	2084.80	2084.36	2083.94	1035.50	904.19	449.94
$A' (cm^{-1})^{b}$	1.3399	1.3384	1.3385	1.3384	1.3432	1.3501	1.3465
5	0.1542	-0.0495	-0.0504	-0.0514	-0.3575	-0.3059	0.2227

^aConstants in the equation $\nu_{sub} = \alpha + \beta K + \gamma K^2$. ^bAssuming B' = B''. ^cAssuming $(A\zeta)' = A'' \times \zeta$.

Ge mass Constant	70 <i>B</i> "	72 <i>B</i> "	74 <i>B</i> ″	72.59 <i>B</i> ″	all A"	
¹² CH ₃ GeH ₃			_	0.28920	1.79246	
¹² CD ₃ GeH ₃	0.23674	0.23574	0.23479	0.23542	1.34251	
¹³ CD ₃ GeH ₃	0.22902	0.22800	0.22703	0.22767	1.34251	

Table 2 Ground-state constants (cm⁻¹) used in perpendicular band analyses

The only other indication of a Fermi resonance occurs in ν_9 of the CD₃ species, where there is a conflict between the ¹²⁻¹³C shift observed and that calculated, which makes for doubt in the assignment of the *Q*-branches in the ¹³C species. This is discussed further below.

The parameters resulting from these new analyses and assignments, all using a quadratic fit, are listed in Table 3.

While data for the perpendicular bands of CH_3GeD_3 are quoted by Griffiths [16], we found it hard to evaluate their reliability, bearing in mind the resolution employed, and no use has been made of these data in the calculations below.

2.2. Parallel bands

No sign of any *Q*-branch due to ν_1 (ν_s CD₃) could be seen where it has been previously reported, near 2073 cm⁻¹ [16,17], under the strong bands due to the ν GeH₃ modes ν_2 and ν_8 , nor has it been observed in the matrix. The best estimate for ν_1 from the SDFTFF is about 2117 cm⁻¹, to which a significant upwards shift must be added owing to Fermi resonance with $2\nu_9$ below.

Q-branch maxima could be resolved for the ⁷⁰Ge, ⁷²Ge and ⁷⁴Ge isotopomers for both ν_4 and ν_5 . These provided the shift data listed in Table 5. Evidence for a Fermi resonance involving v_{\perp} comes from an upwards movement in ν_4 from CH₃GeH₃ to CD₃GeH₃ which is forbidden by the Rayleigh rule. The ${}^{12-13}$ C shifts prove to be eminently compatible with the SDFTFF but the Ge ones are not so. The only obvious source of such a resonance is the A_{\perp} ternary level $\nu_5 + 2\nu_6$ since this will cross over ν_4 between the two species. $2\nu_{12}$, by contrast, remains above ν_4 in both cases. Invoking $\nu_5 + 2\nu_6$, however, involves the difficulty that both ^{13}C and Ge isotopic shifts on ν_5 are larger than those on ν_4 , the former very much more so, and the ¹³C shifts should therefore be much more in conflict with the SDFTFF than the Ge ones, which is not the case. A more likely explanation for the Ge shift anomalies is that hot bands are present in the spectrum which distort the frequencies attributed to the various Ge isotopes. Lower weight is therefore given to the latter, while the 13 C shifts are assumed to be unaffected by such resonance as may be present.

For the species CH₃GeD₃, the only A_1 band centre given any weight was that due to ν_5 , although that due to ν_3 could well have been included. The band due to ν_4 lies on the shoulder of ν_5 and the calculations below gave cause for concern as to the identification of its centre.

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Parameters for perpendicular bands in ¹²CH₃GeH₃ and ¹²CD₃GeH₃ reanalysed in this work

Molecule ^a	¹² CH ₃ GeH ₃	¹² CD ₃ GeH ₃				
Band	$\boldsymbol{\nu}_{10}$	ν_7	Vy	$\boldsymbol{\nu}_{10}$	ν_{12}	
α (cm ⁻¹)	914.055(15)	2243.126(5)	1042.349(11)	906.760(12)	450.839(4)	
β (cm ⁻¹)	3.7632(23)	1.7688(6)	3.2027(11)	3.0417(25)	1.6302(3)	
$10^{3}\gamma ~({\rm cm}^{-1})$	-2.31(28)	-3.34(9)	4.47(18)	8.71(24)	3.92(4)	
$\nu_0 (\mathrm{cm}^{-1})$	911.79	2242.46	1040.26	904.83	450.32	
$A' (cm^{-1})$	1.7901	1.3392	1.3470	1.3512	1.3464	
ζ	-0.2124	0.1634	-0.3648	-0.3017	0.2204	

^aAll parameters calculated for Ge mass of 72.59.

2.3. Torsional mode

Although a number of combination and difference bands involving the torsional mode ν_6 were identified by Griffiths, only two of these were parallel in type, with band centres which may trusted. The latter yield $2\nu_6 = 301 \text{ cm}^{-1}$, so that the value for ν_6 of 155 cm⁻¹ [16] is not likely to be significantly in error. The unscaled DFT calculation gives $\omega_6 = 161.1$, 131.6 and 147.0 for the CH₃, CD₃ and GeD₃ species respectively, so that scaling on 155 cm⁻¹ for the first of these leads to predictions of 126.6 and 141.4 cm⁻¹ respectively for the CD₃ and GeD₃ cases, in the harmonic approximation. Clearly more work requires to be done in the interpretation of the spectra.

3. Theoretical

All QM calculations were carried out in the appropriate symmetry by using the Gaussian 94 program [30]. The DFT functional B3-LYP was used in conjunction with the standard 6-311G** basis set [31.32]. A fine grid was employed consisting of 99 radial shells round each atom and 302 angular points in each shell. Geometry optimisation and vibrational frequency calculations were performed from analytic first and second derivatives, respectively.

The output of Cartesian force constants⁵ together with the corresponding Cartesian coordinates for each atom were fed into the program ASYM40, an update of ASYM20 [33], which permits refinement of scale factors associated with each diagonal symmetry force constant by least-squares fitting to every kind of vibrational datum that stems from the force field. Unlike the program used for the previous work on methylsilane [15], ASYM40 only permits refinement to frequency shifts when these relate to frequencies in the same position in the order of decreasing frequency. Thus we were unable to utilise the small shift that occurs in ν_s SiH₃ from the CH₃ species to the CD₃ one since this mode is ν_2 in the former but ν_1 in the latter, due to a crossing over of the modes (we number all modes in order of diminishing frequency, unlike [15,17]).

Whereas the only Si data used were for the ²⁸Si species, for the germanes we had to input separately data for species with atomic weights 72.59, 70, 72 and 74 so that all kinds of data could be correctly represented. For this purpose ASYM40 had to be expanded to allow for the presence of a total of 13 isotopomers.

As mentioned earlier, a drawback of ASYM40 is that in its scaling procedure each off-diagonal constant is automatically scaled by the geometric mean of the factors for the corresponding diagonal constants.

4. Treatment of data

The observed frequencies and frequency shifts were harmonised by the procedure based on Dennison's rule [34], whereby a factor α is associated with each type of vibration and used to interrelate observed and harmonic frequency according to the equations

 $\nu = \omega(1 - \alpha), \quad \nu' = \omega'(1 - \alpha'), \quad \alpha' = \nu' \alpha / \nu$

for frequencies, in consequence of which

 $\Delta \nu = \Delta \omega (1 - 2\alpha)$

for frequency shifts [35,36]. Here the prime denotes a datum for an isotopic species.

The importance of refining to shifts when adequate weight is being given to ignorance of anharmonicity has been previously emphasised [35,36].

We copy [15] in choosing α values of 0.04, 0.03 and 0.02 for CH stretches, deformations and rocking modes, and 0.03, 0.02 and 0.015 for MH stretches, MH bends and MC stretches, respectively.⁶ With a likely error of \pm 0.01 for each α so chosen, the resulting uncertainty $\sigma_{\Delta \omega}$ in the harmonised shift is given by [35.36]

 $\sigma_{\Delta\omega} = 0.02 \Delta \nu$

Before harmonisation, decisions must be taken as to what if any corrections should be made for Fermi

⁵ The listing of this matrix in the form suitable for direct input into ASYM40 is obtained by including in the command line in the input file the instruction iop(7/33 = 1). The output of transposed atomic polar tensors is found in the archive section of the Gaussian output file, starting at "DipoleDeriv". The axes for these tensors are those for the input Z-matrix, not the "standard" ones.

⁶ One consequence of this choice of anharmonicity factors α was that in the isotopomer CD₃GeH₃, ω_x CD₃ lay above ω_x GeH₃ whereas ν_x CD₃ lies below ν_x GeH₃. This meant that we could not utilise the shift observed in ν_x GeH₃ due to the change CH₃ to CD₃. The only shift of this kind that could be used in the methylgermanes was in ν_x , ν_{ax} GeH₃.

resonances. In addition to the small resonances mentioned above as thought to occur in the $\nu = 1$ levels of ν_4 , either CH₃GeH₃ or CD₃GeH₃ or both, and in ν_{10} of CD₃GeH₃, the universal resonances between ν_s CH₃ and $2\delta_{as}$ CH₃, $2\delta_s$ CH₃ and between ν_s CD₃ and $2\delta_{as}$ CD₃, $2\delta_s$ CD₃, A_1 levels must be expected to be present. Minor ones involving *E* levels of the above overtones with ν_{as} CH₃ and ν_{as} CD₃ levels may also occur [37].

In determining the SDFT force fields, the effects of these resonances were avoided by scaling all the CH stretching constants solely on the basis of the ν^{is} CH values in the partially deuterated species CHD₂MH₃. The same procedure was applied to the scaling of the MH stretching force constants.

A comparison of the CH stretching frequencies from the SDFTFF with those observed then provides the best available estimate of the Fermi resonance shifts on the latter. The calculated SDFTFF frequencies, of course, have first to be deharmonised, which identifies one of the likely sources of error in this procedure, the assumption of identical anharmonicity for the motions represented by ν_s CH₃, ν_{as} CH₃ and ν^{is} CH. The other significant source of error would be that arising in the CH stretch–CH stretch interaction force constant f' determined in the QM force field, which primarily determines the interrelation of these three types of motion, in the local mode approach.

With respect to the ν_4 data for methylgermanes, as mentioned above, the Ge shifts were low weighted compared with the ¹³C ones. The ν_{10} data for CD₃GeH₃, comprising ω , $\Delta \omega$ and ζ , were given no weight at all.

In considering what values to input for the lowest mode ν_{12} , the view has been expressed that the torsional-vibrational interactions present in CH_3SiH_3 require subtraction of about 4 cm^{-1} from the observed band centre for v_{12} for consistency in the resulting force field calculations [38]. Since a detailed analysis of these interactions is only available for one isotopomer of methylsilane to date, it seems inappropriate to correct one species without similar information for the others. No comparable study has been yet made on methylgermanes, where the same effects must be present. For the moment then we have to proceed on the basis of the band centres as determined in the usual way. The effect on the force

field is likely to be only a reduction in the diagonal constant $F_{12,12}$ by about 2%.

In general, all non-shift frequency data were given uncertainties of 1% in recognition of the uncertainty of ± 0.01 in the anharmonicity constant α .

Error in the ζ data stems from two sources: (1) that inherent in a quadratic fit to *Q*-branch maxima; (2) that due to the assumption that $(A\zeta)' = A'' \times \zeta$. It is thought that ± 0.02 comfortably covers both of these.

The vibrational dependence of centrifugal distortion constants is thought to necessitate an uncertainty of at least 5%, but such quantities were only available for methylsilanes. For the latter the decision was taken to use weights identical to those in the recent paper [15], both in the scaling exercise and in the subsequent empirical refinement of the ESDFTFF. For the methylgermanes however, at a stage when certain of the isotope shifts were suspect, these shifts were given lower weight than was afterwards employed for the empirical force field. Thus the scaling was essentially a fit to the CH₃,CD₃ and GeH₃ frequencies and to all the ζ values.

In determining the ESDFT force field, for which the "observed" geometry was employed (Table 4), offdiagonal symmetry force constants from the SDFTFF were gradually replaced by refined force constants to the extent that the latter could be defined. All diagonal constants had to be refined in this process, including that for the $\nu_s CH_3$ symmetry coordinate $F_{1,1}$, which dominates ν_s CH₃ and ν_s CD₃. The procedure was then slightly different for the silanes than for the germanes. For the latter, the "observed" value of $\omega_s CH_3$ was replaced by the estimate of ω from the SDFTFF. However, in methylsilane no such correction was made. This has the consequence that no significance should be given to the value of f' for the CH bond here, which in a valence force field is given by the difference between $F_{1,1}$ and $F_{7,7}$ ($F_{1,1} - F_{7,7} = 3f'$). The best value of the latter in both cases will probably be obtained from the $F_{1,1} - F_{7,7}$ difference in the SDFTFF.

Finally in this section we note that the symmetry coordinates employed are identical to those of [15], except that bending ones are not scaled with a bond length. The κ factors in the δ_s Me and δ_s MH₃ coordinates differ slightly according to the geometry used, DFT or experimental.

Table 4
Observed and calculated geometries for methylsilane and methylgermane

Molecule	rCH (Å)	<i>r</i> MH (Å)	rMC (Å)	(tHCH (°)	αHMH (°)	
CH ₃ SiH ₃ (obs) ^a	1.0957	1.4832	1.8686	108.026	108.423	_
CH ₃ SiH ₃ (calc) ^h	1.0930	1.4872	1.8849	107.954	108.259	
CH ₃ GeH ₃ (obs) ^a	1.0921	1.5285	1.9490	108.841	108.776	
CH ₃ GeH ₃ (calc) ^b	1.0913	1.5390	1.9689	108.623	108.526	
CH ₄ (calc) ^b		1.0907				
SiH ₄ (calc) ^b		1.4838				
$\operatorname{GeH}_{4}(\operatorname{calc})^{\mathrm{b}}$		1.5337				
	$\Delta r_{\rm MH3}$ CH (Å) ^e	$\Delta r_{\rm Me} \rm MH (Å)^c$				_
$CH_3SiH_4(r_a)^d$	0.0023	0.0034				
$CH_3SiH_4(p^{18})^c$	0.0036	0.0037				
$CH_3GeH_3 (r_e)^d$	0.0006	0.0053				
$CH_3GeH_3(\nu^{is})^e$	0.0019	0.0038				

 ${}^{a}r_{0}$ geometry used in this work.

 ${}^{b}r_{e}$ geometry from the tz DFT calculation.

[®]Difference MeMH₃ – CH₄ or MH₄.

^dFrom the tz DFT-based r_e values in this work.

"From the correlations between r_0 and ν^b CH [19], ν^b SiH [20] and ν^b GeH [21], respectively.

5. Results: geometries, force fields and fit to data

5.1. Geometries

Table 4 compares the calculated and observed geometrical parameters for methylsilane and methylgermane. Included in this table are the lengthenings which are calculated for the SiH or GeH bond on substitution of methyl into the parent MH₄ molecule. These are compared with the estimates derived from the ν^{is} values in the four molecules [19-21]. The agreement is good for the silanes and quite so for the germanes. The DFT calculation makes the CH bond in methylsilane shorter by 0.0027 A than that in methylgermane. This is a larger difference than that obtained previously in the SCF calculation of Hein et al., 0.001 Å [18]. The shortening predicted from the ν^{is} values is 0.0017 Å. The lengthening in $r_{\rm e}$ CH from CH_4 to MeMH₃ is consistently smaller than that predicted from ν^{is} .

Both r_eMH and r_eMC are calculated to be longer than the experimental r_0 values. This parallels the tendency of DFT calculations to predict stretching force constants lower than those observed. Observed and calculated bond angles agree within 0.25°.

5.2. Force field and fits to data: methylgermanes

The fit to observed data obtained with the SDFTFF for methylgermane is shown in column 6 of Table 5 $[\epsilon(1)]$, while the two force fields are shown in Table 6. The ϵ values for ω_1 in the CH₃ and CD₃ species (19.6 and 12.6 cm⁻¹, respectively) yield estimates for the Fermi resonance shifts on the bands concerned of about 18.8 and 12.2 cm⁻¹, which are eminently reasonable for this kind of resonance. A similar shift is found on ω_1 of the GeD₃ species. The only other frequencies poorly fitted are ω_{11} in the ¹²CD₃GeH₃ species and ω_4 and ω_{12} in the CH₃GeD₃ one.

The only frequency shifts in significant error are those for ω_4 and ω_5 in the ⁷⁴Ge species in both CD₃ isotopomers, ¹²C and ¹³C.

All the ζ s are comfortably fitted within the uncertainties allocated except for ζ_{10} in the 12 CD₃ and 13 CD₃ species, where resonance is suspected with $2\nu_{12}$.

In the empirical refinement, with SDFT constraints, the number of off-diagonal constants which could be released were four in the A_1 block and eight in the *E*. Of these, only two in the A_1 , $F_{1,2}$ and $F_{3,5}$, and one in the *E* block. $F_{7,9}$, are different by more than one standard deviation from their SDFT values. Of a number of small changes in the fit, the most marked is the improvement in that to v_{11} in 12 CD₃GeH₃. There

Table 5				
Comparison of observed	and calculated	data for	methylgermane	species

¹² CH ₃ GeH ₃						
Mode	Ge species	$\nu/\Delta \nu^{a}$	$\omega/\Delta\omega^b$	σ	$\epsilon(1)^d$	$\epsilon(2)^d$
1	72.59	2939.0	3041.9°	30.4	19.57 [†]	1.56
2	72.59	2086.4	2150.93	21.5	1.74	-0.43
3	72.59	1254.9	1293.71	12.9	2.87	3.59
4	70	843.40	860.61	8.6	-1.05	-1.67
4	72	0.36	0.37	0.1	0.08	-0.01
4	74	0.75	0.78	0.2	0.22	0.04
5	70	605.9	615.13	6.2	1.96	-0.83
5	72	1.5	1.55	0.1	0.04	0.10
5	74	2.9	2.99	0.2	0.05	0.16
7	72.59	2998.73	3123.65	31.2	0.91	2.39
8	70	2085.23	2149.72	21.5	-1.77	-0.23
8	72	0.45	0.48	0.05	-0.01	0.00
8	74	0.88	0.93	0.05	-0.02	0.00
9	72.59	1430	1474.23	14.7	1.69	1.11
10	72.59	911.79	930.40	9.3	0.16	-0.18
11	72.59	850	867.30	8.7	1.62	-1.76
12	72.59	505.77	516.09	5.2	1.89	3.96
Mode	Ge species		۲ ^۴	σ^{c}	$\epsilon(1)^{d}$	$\epsilon(2)^d$
7	72.59		0.0655	0.05	0.0161	0.0131
8	70		-0.0519	0.02	-0.0027	-0.0009
8	72		-0.0521	0.02	-0.0022	-0.0004
8	74		-0.0531	0.02	-0.0026	-0.0008
9	72.59		n.o.	n.w.	-0.2899*	-0.3004*
10	72.59		-0.2124	0.02	0.0026	-0.0023
11	72.59		n.o.	n.w.	0.3174*	0.3278*
12	72.59		0.2640	0.02	-0.0038	0.0010
¹² CD ₃ GeH ₃						
Mode	Ge species	$\nu/\Delta \nu^{\rm a}$	$\omega/\Delta\omega^{ m b}$	σ^{c}	$\epsilon(1)^{d}$	$\epsilon(2)^d$
1	72.59	2072.8	2181.0°	21.8	12.56	-1.11
2	72.59	2087.2	2151.75	21.5	2.68	0.51
3	72.59	978.2	1001.62	10.0	-2.76	-2.77
4	70	845.72	862.78	8.6	1.19	1.22
4	72	0.50	0.53	0.5	0.24	0.19
4	74	1.05	1.10	0.5	0.54	0.43
5	70	553.3	560.98	5.6	1.62	-0.45
5	72	1.6	1.64	0.3	0.09	0.13
5	74	3.3	3.39	0.5	0.37	0.45
7	72.59	2242.46	2311.61	23.1	-1.63	1.10
8	70	2084.84	2149.31	21.5	-1.74	-0.22
8	70 ^h	0.39	0.41	0.05	0.00	0.00
8	72	0.45	0.48	0.05	-0.01	0.00
8	74	0.87	0.93	0.05	-0.02	-0.01
9	72.59	1040.26	1063.47	10.6	-1.07	-0.87
10	72.59	904.83	923.16	n.w.	0.92	-1.71
11	72.59	713.2	725.2	7.3	-9.01	1.09
12	72.59	450.32	458.48	4.6	2.99	-2.84

Table 5
Continued

			ζ	σ	$\epsilon(1)$	$\epsilon(2)$
7	72.59		0.1634	0.02	-0.0043	-0.0055
8	70		-0.0509	0.02	~0.0020	-0.0001
8	72		-0.0518	0.02	-0.0023	0.0003
8	74		-0.0522	0.02	-0.0020	-0.000}
9	72.59		-0.3648	0.02	-0.0077	0.0001
10	72.59		-0.3017	n.w.	-0.0606	-0.0820
11	72.59		n.o.	n.w.	0.3438*	0.3327*
12	72.59		0.2204	0.02	-0.0025	-0.0020
¹³ CD ₃ GeH ₃						* <u>****</u> *******************************
Mode	Ge species	$\Delta \nu^{i}$	$\Delta \omega^{i}$	σς	$\epsilon(1)^d$	$\epsilon(2)^{d}$
1	72.59	n.o.	n.o.	n.w.	4.75*	5.01*
2	72.59	n.o.	n.o.	n.w.	0.00*	$(0.00)^{*}$
3	72.59	13.6	14.3	0.3	-0.22	0.01
4	70	0.30	0.32	0.1	0.04	0.01
4	72	0.81	0.84	0.5	0.26	0.16
4	74	1.33	1.38	0.5	0.53	0.38
5	70	9.48	9.73	0.2	-0.02	-0.07
5	72	11.07	11.37	0.2	0.03	0.03
5	74	12.50	12.84	0.2	-0.01	0.02
7	72.59	14.76	15.70	0.5	-0.34	-0.09
8	70	0.04	0.05	0.05	0.03	0.04
3	72	0.48	0.52	0.05	0.01	0.02
8	74	0.90	0.96	0.05	-0.01	0.00
.)	72.59	4.76	4.98	n.w.	1.62	1.68
10	72.59	0.64	0.68	n.w.	0.60	().64
11	72.59	n.o.	n.o.	n.w.	4.89*	5.20*
12	72.59	0.38	0.39	0.05	-0.15	-0.03
			5	σ	<i>ε</i> (1)	<i>ε</i> (2)
7	72.59		0.1542	0.02	0.0035	-0.0021
к	70		-0.0495	0.02	-0.0006	0.0013
8	72		-0.0504	0.02	-0.0009	0.0011
8	74		-0.0514	0.02	-0.0012	0.0007
9	72.59		-0.3575	0.02	0.0104	-0.0025
10	72.59		-0.3059	n.w.	-0.0653	-0.0866
11	72.59		n.o,	n.w.	0.3455*	0.3348*
12	72.59		0.2227	0.02	-0.0020	-0.0014
¹² CH ₃ GeD ₃						

Mode	Ge species	ν ⁱ	ω	σ	$\epsilon(1)$	$\epsilon(2)$	
1	72.59	2933.2	3055.4	n.w	13.5	15.1	
2	72.59	1496.2	1529.1	n.w	5.2	3.7	
3	72.59	1252.8	1291.5	n.w	1.4	2.3	
4	72.59	627	636.5	n.w.	17.3	10.7	
5	72.59	598	607.0	6.1	-3.1	~0.1	
7	72.59	2993	3117.7	n.w.	-5.0	-3.5	
8	72.59	1500	1533.1	n.w.	-0.5	0.7	
9	72.59	1422	1465.7	n.w.	-6.7	-7.3	
10	72.59	830	846.5	n.w.	1.1	-5.7	

J	υ	4	

Та	ble	5	
~			

Continued							
¹² CH ₃ GeD	3						
11 12	72.59 72.59	658 382	648.6 387.9	n.w. n.w.	-4.4 -7.1	-7.7 -2.1	
					$\zeta_{\rm calc}(1)$	$\zeta_{cale}(2)$	
7	72.59				0.0494	0.0524	
8	72.59				0.0280	-0.0297	
9	72.59				-0.2892	-0.2998	
10	72.59				0.2924	0.2988	
11	72.59				-0.2114	-0.1996	
12	72.59				0.3084	0.3009	

^aObserved frequency (ν in cm⁻¹) or frequency shift ($\Delta \nu$ in cm⁻¹) ⁷⁰Ge-⁷²Ge or ⁷⁰Ge-⁷⁴Ge, from [14,16], with reassignments as discussed in the text.

n.o. = no observation.

^bHarmonic frequency or frequency shift (cm⁻¹).

^cUncertainty in datum. n.w. = no weight.

^dError vector obs-calc for: (1) the SDFT force field; (2) the ESDFT force field. Asterisks indicate the calculated value where there is no observation.

""Best" estimate of ω_1 from the SQM calculation.

⁶The obs-calc value in the SQM calculation when ω_{obs} is taken to be the harmonised observed frequency. The ϵ value therefore represents the likely Fermi resonance correction on ω_1 .

^gZeta data derived assuming $(A\zeta)' = A'' \times \zeta$.

^hShift from ¹²CH₃⁷⁰GeH₃.

Shifts from ¹²CD₃⁷⁰GeH₃, all from this work.

Data from [16].

is no sign of any error resulting from the reassignment of the centre of ν_{10} in CH₃GeH₃ to 911.79 cm⁻¹.

The only frequency in CH₃GeD₃ accorded weight in either refinement was v_5 and this is well fitted in both cases. ν_4 in the ESDFTFF however is still poorly predicted, with an ϵ value of 10.7 cm⁻¹. The proximity of ν_4 and ν_5 means that each is a coupled ν GeC and δ_5 GeD₃ motion, and the consequent splitting is determined by F_{35} . The latter is well defined by both frequencies and frequency shifts in the other species, and the splitting reported by Griffiths of about 30 cm⁻¹ cannot be reproduced. If the values of ω_4 and ω_5 are weighted highly, e.g., $\pm 1 \text{ cm}^{-1}$, ω_4 in CH₃GeH₃ and CD₃GeH₃ promptly moves up by $11-14 \text{ cm}^{-1}$. It is unlikely that our failure to reproduce this ν_4/ν_5 splitting in CH₃GeD₃ is the result of the anharmonicity corrections which have been applied, as these fortuitously are identical.

In the absence of any resonance which could affect ν_4 and not ν_5 , we have to conclude that the band centre of ν_4 in this species has not yet been identified correctly. The ϵ values of 6-8 cm⁻¹ for ω_9 , ω_{10} and ω_{11} in CH₃GeD₃ will include some contribution from the anharmonicity corrections, but probably are mainly due to the absence of any K structure analyses for the perpendicular bands concerned.

The ESDFTFF has no more success than the EDFT one in fitting the ⁷⁴Ge shifts on ω_4 and ω_5 in the ¹²C and ¹³C CD₃ species and this strengthens our belief that these data are suspect.

The ¹³C shift on ν_9 in ¹³CD₃GeH₃ bears on the assignment of the *Q*-branches in this band. With the assignment adopted in Table 1, the ϵ value for $\Delta \omega_9$ is unreasonably high, 1.70 cm⁻¹ in the ESDFTFF. If ^{*R*}*Q*₀ is moved up by one *Q*-branch to 1040.74 cm⁻¹, the shift $\Delta \nu_9$ becomes 1.51 cm⁻¹ instead of 4.76 cm⁻¹, and the $\epsilon_{\Delta\omega}$ value is equally poor but in the opposite direction, -1.70 cm⁻¹. Two resonances may be responsible for this anomaly, those with $\nu_5 + \nu_{12}$ and $\nu_6 + \nu_{10}$ respectively. The former has a calculated shift of about 9.9 cm⁻¹ and the latter one of about 0.6 cm⁻¹. The extent of resonance would much less if ν_9 had to

Table 6 Force fields for methylsilane and methylgermane^a

		Methylsilane			Methylgerman	ne
		SDFT ^b	ESDFT	ESAI ^d	SDFT ^b	ESDFT
A						
\vec{F}_{11}	ν CH :	5.3019	5.3557(386)	5.349(33)	5.3541	5,3441(247)
F_{12}	•	0.1393	0.0652(200)	0.038(36)	0.1527	0.0972(312)
F_{13}		0.0603	0.0603	0.056	0.0479	0.0479
F_{14}		0.0045	0.0045	0.012	0.0014	0.0014
$F_{1.5}$		-0.0141	-0.0141	-0.018	-0.0162	-0.0162
F 2.2	δ _{CH3}	0.4729	0.4741(38)	0,474(4)	0.4891	0.4898(20)
$F_{2,3}$		-0.1875	-0.1807(22)	-0.173(4)	-0.2137	-0.2112(35)
$F_{2.4}$		-0.0201	-0.0201	-0.021	-0.0238	0.0238
F 2.5		0.0205	0.0207(10)	0.021(8)	0.0255	0.0262(10)
$F_{3,3}$	νMC	2.9794	3.0062(164)	3.038(14)	2.7828	2.7902(119)
F 3,4		0.0784	0.0784	0.087	0.0554	0.0554
F_{35}		-0.1313	-0.1413(87)	-0.132(7)	-0.1354	-0.0904(49)
$F_{4,4}$	$\nu_{s}MH_{3}$	2.9276	2.9491(208)	2.947(14)	2.7292	2.7350(118)
$F_{4,5}$		0.0498	0.0498	0.055	0.0730	0.0730
Fss	δ_MH	0.5372	0.5383(42)	0.535(4)	0.4924	0.4907(20)
E						
$F_{7,7}$	$\nu_{as}CH_3$	5.1973	5.1622(426)	5.204(29)	5.2532	5.2562(346)
F 7.8		-0.1474	-0.1169(85)	-0.146(8)	-0.1502	-().1446(72)
F 7.9		0.1249	0.1249	0.089(22)	0.0996	0.1633(350)
F _{7.10}		-0.0133	-0.0133	-0.012	-0.0158	-0.0124(26)
$F_{7,11}$		-0.0119	-0.0119	-0.013	-0.0082	-0.0082
$F_{7,12}$		0.0379	0.0379	0.034	0.0274	0.0274
$F_{8,8}$	δ _{as} CH ₃	0.5533	0.5482(62)	0.555(10)	0.5571	0.5551(36)
F 8.9		0.0226	0.0463(97)	0.022(10)	0.0191	0.0191
$F_{8\pm0}$		0.0025	0.0025	0.000	0.0009	0.0009
F_{841}		-0.0084	-0.0084	-0.008	-0.0062	-0.0062
$F_{8,32}$		0.0000	0.0000	-0.008(16)	0.0018	0.0018
$F_{0,0}$	ρCH_3	0.4149	0.4258(79)	0.417(11)	0.4443	0.4643(45)
Futo		0.0256	0.0256	0.026	0.0305	0.0305
F_{2211}		-0.0236	-0.0225(55)	-0.018(3)	-0.0195	-0.0148(36)
$F_{2,12}$		0.1671	0.1622(33)	0.107(11)	0.1613	0.1445(32)
F 10,10	$\nu_{\rm as} \rm MH_{2}$	2.8376	2.8437(193)	2.836(15)	2.6999	2.6960(169)
$F_{10,11}$		-0.0689	-0.0594(81)	0.058(6)	-0.0930	-0.0944(35)
$F_{10,12}$		0.0663	0.0746(513)	0.053(7)	0.0820	0.0973(167)
$F_{11,11}$	$\delta_{as}MH$	0.4894	0.4875(51)	0.495(2)	0.4766	0.4773(66)
$F_{11,12}$		-0.0739	-0.0763(102)	-0.095(4)	-0.0539	-0.0581(79)
$F_{12,12}$	$ ho MH_3$	0.5475	0.5406(77)	0.546(8)	0.5277	0.4841(56)

^aUnits: aJ Å⁻²; aJ Å^{-t} rad^{-t}; aJ rad⁻².

^hScaled DFT force field.

"Empirical/scaled DFT force field.

^dEmpirical/scaled *ab initio* force field from [15], with a change to unscaled bending symmetry coordinates.

gain about 1.6 cm⁻¹ from $\nu_5 + \nu_{12}$, than if it were to lose 1.6 cm⁻¹ to the level $\nu_6 + \nu_{10}$. This is the reason for our choice of ${}^{R}Q_0$ at 1035.50 cm⁻¹ in 13 CD 3GeH 3.

The CH₃/CD₃ shift on ν_{as} GeH₃ (ν_8) is of interest as it is fitted exactly by both the SDFT and ESDFT force

fields. The parameter which defines it is $F_{7,10}$, the $\nu_{as}CH_3/\nu_{as}GeH_3$ interaction constant. If this datum is omitted from the ESDFT refinement, $F_{7,10}$ doubles in size from the EDFT to the ESDFT force field. With the datum, the two values agree very well. This particular interaction is therefore well reproduced by

 Table 7

 Comparison of observed and calculated data for methyl silanes

Mode	¹² CH ₃ SiH	¹² CH ₃ SiH ₃						¹³ CH ₃ SiH ₃				
	ω	σ	$\epsilon(1)^a$	$\epsilon(2)^{a}$	$\epsilon(3)^a$	$\Delta \omega^{h}$	σ	$\epsilon(1)^{a}$	$\epsilon(2)^{\mathfrak{d}}$	$\epsilon(3)^a$		
1	3048.86	30	19.03	0.44	1.43	3.63	0.20	0.39	-0.04	0.03		
2	2236.86	22	3.17	-4.82	-3.82	0.05	0.20	0.05	0.05	0.05		
3	1289.35	13	0.13	-1.56	-2.05	9.77	0.05	0.01	-0.01	-0.02		
4	957.52	10	-2.73	-2.71	-0.35	0.10	0.10	0.10	0.10	0.10		
5	710.09	7	4.89	1.93	-1.12	14.40	0.05	0.04	0.01	0.02		
7	3105.90	31	2.73	11.52	-0.62	10.76	0.25	-0.27	-0.42	-0.30		
8	2232.76	22	-0.97	-3.29	-0.75	0.03	0.05	0.03	0.03	0.03		
9	1461.86	15	2.27	-4.39	1.82	3.05	0.50	0.64	1.06	0.48		
10	967.00	10	2.51	1.95	-0.30	0.20	0.50	0.15	0.17	0.20		
11	889.93	9	-3.71	0.96	-0.32	6.53	0.35	0.21	-0.02	0.22		
12	531.98	5	3.73	0.97	0.18	0.05	0.10	0.00	-0.01	0.00		
7	5	σ	<i>ϵ</i> (1)	<i>ϵ</i> (2)	<i>ϵ</i> (3)	5	σ	ε(1)	<i>ϵ</i> (2)	<i>ϵ</i> (3)		
/	0.063	0.02	0.014	-0.003	0.006	0.063	0.02	0.024	0.007	0.016		
8	0.009	0.02	0.001	-0.007	0.004	0.011	0.02	0.003	-0.005	0.006		
9	-0.359	0.02	-0.054	-0.027	-0.022	-0.331	0.02	-0.031	-0.004	0.001		
10		-	-0.259*	-0.256*	-0.243*			-0.257*	-0.255*	-0.242*		
11	0.368	0.02	0.007	0.005	0.006	0.367	0.02	-0.003	0.004	0.006		
12	0.243	0.02	0.001	0.001	-0.010	0.245	0.02	0.003	0.003	-0.010		
	D	σ	ε (1)	<i>ϵ</i> (2)	$\epsilon(3)$	D	σ	<i>ϵ</i> (1)	<i>ϵ</i> (2)	<i>ϵ</i> (3)		
D_{I}	10.71	0.53	0.46	0.10	-0.18	10.82	0.66	1.15	0.80	0.62		
D_{IK}	45.55	2.28	2.02	0.38	-1.35			41.3*	42.9*	43.3*		
Dĸ			154*	152*	137*	-		156*	155*	141*		
Mode	¹² CH ₃ SiD	3				¹² CD ₃ SiH	13					
	$\omega, \Delta \omega^{b}$	σ	<i>ϵ</i> (1)	<i>ϵ</i> (2)	$\epsilon(3)$	$\omega, \Delta \omega^{h}$	σ	<i>ϵ</i> (1)	<i>ϵ</i> (2)	$\epsilon(3)$		
ļ	3045.71	30	15.89	-2.70	-1.70	-0.25	n.w. ^c	-0.28	-0.26	-0.05		
2	1598.56	16	8.25	2.72	3.85	2194.8	22	19.7	2.5	-3.2		
3	0.51	0.05	-0.03	0.00	-0.05	1020.2	10	2.6	2.0	1.2		
4	748.95	7	0.95	2.01	-1.38	955.3	10	-1.2	-1.9	1.4		
5	661.96	7	4.88	1.15	2.68	648.9	6	3.5	2.0	0.2		
7	0.00	0.10	-0.03	-0.03	-0.03	2304.1	23	6.9	11.7	0.7		
8	1617.95	16	4.06	2.22	3.63	0.85	1.0	0.14	0.04	0.24		
9	0.85	0.50	0.57	0.48	0.44	1059.4	11	4.7	3.3	7.3		
10	841.31	8	-4.31	-0.71	-0.33	971.6	20	8.4	7.7	2.5		
11	695.10	7	3.74	3.02	1.90	786.9	8	2.9	5.9	-1.2		
12	420.0	4	-0.64	-2.30	1.71	463.0	15	11.2	8.2	9.0		
	5	σ	<u>ε(1)</u>	<i>ϵ</i> (2)	<i>ϵ</i> (3)	<u>`</u>	σ	<i>ϵ</i> (1)	<i>ϵ</i> (2)	<i>ϵ</i> (3)		
7	0.056	0.02	0.007	-0.010	0.002			0.163*	0.178*	0.171*		
8	0.088	0.02	0.020	0.012	0.101			0.010*	0.018*	0.006*		
9	-0.346	0.02	-0.041	-0.013	0.003	-	-	-0.367*	-0.393*	-0.385*		
10	0.346	0.02	0.004	-0.009	0.003			-0.249*	~0.249*	-0.191*		
11	-0.277	0.02	-0.002	0.001	-0.008			0.336*	0.337*	0.273*		
12			0.260*	0.258*	0.253*			0.216*	0.220*	0.239*		

Mode	¹² CH ₃ SiI)3				¹² CD ₃ S	6iH 3			
	D		<i>ϵ</i> (1)	<i>ϵ</i> (2)	<i>ϵ</i> (3)			<i>ϵ</i> (1)	<i>ϵ</i> (2)	e(3)
D_J D_{III}			7.2* 44.4*	7.5* 46.1*	8.2* 41.4*	_		6.9* 21.1*	7.1* 21.1*	7.5* 37.9*
D_K	_	-	40.9*	38.6*	22.9*	-		78.0*	79.1*	65.3*
Mode	¹² CD ₃ SiI	D ₃	<u> </u>							
	ω . $\Delta \omega^d$	σ	ε(1)	<i>ϵ</i> (2)	<i>ϵ</i> (3)					
1	-2.1	n.w.`	-1.8	-1.6	-1.7					
2	1596.5	16	6.4	0.9	- 2 .1					
3	1017.1	10	2.5	1.4	1.3					
4	725.3	7	-0.2	1.1	0.7					
5	622.5	6	4.5	1.7	1.9					
7	1.1	1.0	2.2	0.2	0.4					
8	1615.4	16	1.5	-0.3	1.1					
9	1051.3	20	-2.6	-3.9	2.6					
10	701.4	7	-2.3	-2.5	-6.1					
11	677.5	7	-8.4	-7.2	-5.0					
12	393.4	15	14.0	12.01	13.4					
	5		$\epsilon(1)$	<i>ϵ</i> (2)	<i>ϵ</i> (3)					
7		_	0.165*	0.180*	0.172*					
8		-	0.068*	0.075*	0.070*					
9			-0.369*	-0.395*	-0.392*					
10			0.250*	0.210*	0.236*					
11	·		-0.190*	-0.144*	-0.157*					
12	-		0.218*	0.218*	0.222*					
	D		$\epsilon(1)$	$\epsilon(2)$	$\epsilon(3)$					
D_J			5.0*	5.1*	5.6*					
D_{JK}			17.8*	18.4*	31.0*					
D _k			29.1*	28.5*	16.0*					

^aError vector obs-calc: (1) scaled DFT force field; (2) empirical/scaled DFT force field; (3) ESAIFF, [15].

^b $\Delta\omega$ relative to ¹²CH₃SiH₃. Mode numbering in order of decreasing frequency, contrary to [15].

 $\sigma_{\Delta\omega} = 1.0 \text{ cm}^{-1} \text{ in [15]}.$

 ${}^{d}\Delta\omega$ relative to ${}^{12}\text{CD}_3\text{SiH}_3$.

 $^{\circ}\sigma_{\Delta\omega} = 2.0 \text{ cm}^{-1} \text{ in [15]}.$

the QM calculation, which for a constant linking two different groupings is pleasing.

There remains the problem of the three constants mentioned above which differ in the SDFT and ESDFT force fields. It is probably premature to assert that these discrepancies are not due to problems still lurking in the observed data and that the SDFT force field is deficient in respect of these constants. Apart from the obvious need for high-resolution work on the perpendicular bands in all the species studied, additional data from ¹³CH₃GeH₃ would be very valuable.

5.3. Force field and fit to data: methylsilanes

Although more data and more kinds of data are available for the silanes than for the germanes, the problems in fitting them appear to be greater, as seen in the comparison in Table 7, where $\epsilon(1)$, $\epsilon(2)$ and $\epsilon(3)$ are the error vectors for the SDFT, ESDFT and previous ESAI [15] force fields, respectively.

Starting with the errors on ω_1 (ν_x CH₃), these are very similar in the SDFTFF to those in methylgermanes, indicating very similar Fermi resonance corrections due to $2\delta_{as}CH_3$ below. The extent of the resonance appears to diminish slightly in CH₃SiD₃. Elsewhere there is serious failure on the part of both SDFT and ESDFT force fields to predict ω_{12} in the CD₃SiH₃ and CD₃SiD₃ species. This reinforces the evidence from [15] that the band centres reported earlier by Clark and Drake [39] are incorrect.

A number of shifts are poorly reproduced by the SDFTFF, including six ¹³C ones and three of the other kind. Only two of the ¹²C shifts, those on ω_1 and ω_{11} , are improved in the ESDFTFF and the improvement for ω_1 is likely to be illusory in view of the resonance involved on ν_1 . Of the other shifts, those on ω_8 for ¹²CD₃SiH₃ and ω_7 for ¹²CD₃SiD₃ are better in the ESDFTFF while those on ω_1 in these two species are probably again susceptible to resonances. Perhaps more serious is the inability of the SDFTFF to reproduce the values of ζ_9 in ¹²CH₃SiH₃ and ¹³CH₃SiH₃. The error here is substantially reduced in the ESDFTFF in the former case and entirely in the latter.

A curious feature of the ESDFTFF was the tendency of $F_{7,9}$ to move to the unacceptably high value of 0.291 aJ $Å^{-1}$ rad⁻¹ if this constant were allowed to refine. The driving force for this appeared to be the ¹³C shift on ω_9 . Unlike the ESAIFF of [15], we were therefore obliged to constrain $F_{7,9}$ to its SDFT value. It is of interest that $F_{7,9}$ also tends to increase from the SDFT to the ESDFT force fields in the case of methylgermane, but not by such a large amount. The total number of off-diagonal constants released was then 22, nine in the A_1 and 13 in the E block, compared with nine and 14 respectively in the ESAIFF [15]. The ESDFT and ESAI force fields are then only strictly comparable in the A_{\perp} species, where the only deviation concerns the poorly determined $F_{1,2}$. The tendency of this constant to diminish from the SDFT to the ESDFTFF in both silane and germane may be linked to the absence of hard information on ν_1 , due to Fermi resonance. Why $F_{7,8}$ should fall in our ESDFTFF when it remains constant in the ESAIFF and in the germanes is not clear. A reappraisal of the weighting on the data is probably needed. It would certainly be premature to suspect error in the DFT constants at this stage.

Looking at the constrained constants in the ESDFT and ESAI force fields the overall agreement is good, suggesting that there is little to choose between the DFT and double- ζ SCF approaches.

The main differences between the present results for methylsilane and the previous ones [15] lie in the prediction of unobserved centrifugal distortion constants. These arise from the transcription error mentioned above, which affected only the *D*s.

Taking the two molecules together, we feel that the DFT calculations are successful in identifying likely errors in band centres and also pointing up effects of resonances both suspected and unsuspected through failure to fit Coriolis and frequency shift data.

5.4. Scale factors

These are summarised for methylsilane and methylgermane in Table 8 together with similar factors for CH_4 , SiH_4 and GeH_4 , the latter determined simply from the harmonised frequencies of the parent molecule. The variations are interesting.

Amongst the stretching coordinates, different types of stretch in SiH₄ and GeH₄ are quite well fitted by a single scale factor, the values for which are close to the single ones determined in the methyl compounds, with just a modest rise from SiH to GeH, which may reflect erroneous estimates of the extent of anharmonicity. A much bigger rise in factor is needed from SiC to GeC. The DFT treatment is therefore markedly poorer for the GeC bond, as measured by the departure of the factor from unity. In the SCF/ECP treatment of Hein *et al.*, the reverse is true.

Amongst the bending coordinates, the factors for δ_{s} CH₃, δ_{as} CH₃ and ρ CH₃ could have been constrained equal with little loss in quality of fit, but those for $\delta_{s}MH_{3}$, $\delta_{as}MH_{3}$ and ρMH_{3} are significantly different from each other, particularly for the germane compound. Even in GeH₄ itself there is evidence of a need for varying factors according to different types of bending motion. The source of the latter variation may in part lie in inappropriate anharmoncity corrections, but this is unlikely to be a major reason for the variations in methylsilane and methylgermane. The fact that these do not follow any simple trend, common to both Si and Ge, means that it would be unwise to predict in advance any variation that might be found in a compound of apparently similar structure, at this level of theory. Each case will need to be treated on its merits.

Motion	Symmetry	MeSiH ₃		MeGeH ₃		
	coordinaces	DFT/6-311G***	SCF/ECP ^b	DFT/6-311G***	SCF/ECP ^b	
vCH ^c	1,7	0.9988	0.8361	0.9999	0.8411	
νMH ^c	4.10	1.0100	0.8344	1.0253	0.8808	
νMC	3	1.0218(95)	0.9110	1.0834(34)	0.9442	
δ _{CH}	2	0.9765(100)	0.7758	1.0062(38)	0.8021	
δ,MH;	5	1.0455(65)	0.8297	1.0296(37)	0.8389	
δ _{as} CH	8	0.9882(110)	0.7758	0.9997(37)	0.8021	
ρCH ₃	9	0.9790(156)	0.7758	0.9963(68)	0.8021	
δ _{as} MH	11	0.9974(99)	0.8297	1.0583(56)	0.8389	
ρMH ;	12	1.0280(146)	0.8297	1.0959(79)	0.8389	
τ^{d}	6	0.9507	0.9639	0.9257	0.7927	
Motion/symme	etry	CH ^c ₄	SiH₄		GeH ₄	
		DFT/6-311G***	DFT/6-311G** ^{a.c}	SCF/ECP ^b	DFT/6-311G** ^{a.e}	SCF/ECP ^h
vCH, vMH	A1	1.0088	1.0144	0.8299	1.0301	0.8860
vCH, vMH	F_2	1.0081	1.0093	0.8299	1.0260	0.8860
δCH, δΜΗ	Ē	1.0252	1.0235	0.7926	1.0434	0.8157
δCH, δMH	F_2	1.0144	1.0246	0.7926	1.0274	0.8157

Table 8 Scale factors for the DFT/6-311G** force fields of MeSiH₃, MeGeH₃, CH₄, SiH₄ and GeH₄

"This work.

^b[18], scaled on observed frequencies.

Exact fit to the ω^{i_5} values (cm⁻¹): MeSiH₃, CH 3080.37, SiH 2233.56; MeGeH₃, CH 3097.78, GeH 2149.52 (harmonised from observed values in [20,21]).

^dExact fit to τ values: CH₃SiH₃ 190 cm⁻¹; CH₃GeH₃ 157 cm⁻¹.

*Exact fit to harmonised frequencies of the CH₄ or MH₄ species, α values as for MeMH₃. Data from references in [40].

5.5. Electrical properties

Table 9 gives the atomic polar tensor elements for representive atoms in each of the five molecules studied. For the hydrogen atoms only, the z axis is along the bond concerned. The y axis is then at right angles to the H–C–M plane. Included amongst the DFT results are some for MeSiH₃ obtained by an SCF/6-31G* approach.

Table 10 lists the Mulliken atomic and King effective atomic charges q and χ , the mean atomic dipole moment \vec{P} , tensor anisotropy β and charge undeformability parameter \vec{P}/β , all for the hydrogen atoms concerned. Also included are the dipole derivatives $d\mu/dr$ for the CH and MH bonds involved. A feature noted before in experimental studies of the MH₄ compounds is that although $d\mu/dr$ is larger in GeH₄ than in SiH₄, the MH bending moment is larger in silane [40], in line with the increased negative Mulliken charge there. This results in the King effective atomic charge for the H atom being larger

in SiH₄ than in GeH₄. The charge undeformability \bar{P}/β is correspondingly greater for H in SiH₄ than it is for H in GeH₄. \bar{P}/β is much smaller in CH₄ principally because the diagonal elements of the tensor have different signs, $d\mu/dr$ being negative while μ/r is positive.

These trends are repeated in the methyl compounds. $d\mu/dr$ for the GeH bond is higher than it is for the SiH one, but χ is larger in methylsilane. The SiH bending moments must therefore be higher in the latter, as in fact can be seen by inspecting the diagonal elements of the tensors in Table 9. (The bond length factor in the latter only varies by 3.5% from SiH to GeH.) These elements also show that the bending moment is more negative in the x direction than it is in the y one, a trend which occurs for all three types of bond, even though the sign of the moment is negative for SiH and GeH but positive for CH.⁷

The inductive effect of methyl substitution on the

⁷ This trend appears also in ethane [41].

Atom		MeSiH ₃						MeGeH ₃			
		DFT/6-311G**			SCF/6-31	SCF/6-31G*			DFT/6-311G**		
		∂x	дy	∂z	д <u>х</u>	ду.	∂z	dx	дy	дz	
$H(C)^a$	$\partial \mu_x$	0.052	0	-0.020	0.059	0	0.021	0.021	0	-0.030	
	$\partial \mu_{y}$	0	0.090	0	0	0.081	0	0	0.080	0	
	$\partial \mu$	-0.050	0	-0.116	0.055	0	-0.149	0.066	0	~0.116	
H(M) ^a	$\partial \mu_{\lambda}$	-0.276	0	-0.028	-0.327	0	0.025	-0.243	0	-0.034	
	$\partial \mu_{y}$	0	-0.227	0	0	-0.283	0	0	-0.198	0	
	∂μ_	-0.006	0	-0.328	0.012	0	-0.432	-0.002	0	-0.359	
C ^ħ	$\partial \mu_{x,y,z}$	-0.235	-0.235	-0.413	-0.231	-0.231	-0.411	-0.200	-0.200	-0.271	
M^{h}	$\partial \mu_{x,y,z}$	1.013	1.013	1.272	1.289	1.289	1.447	0.979	0.979	1.156	
		CH₄			SiH ₄			GeH₄			
		dx	<i>∂y</i>	∂z	д <i>х</i>	дy	дz	∂x	<i>∂y</i>	<i>∂z</i>	
H ^c	∂μ _{x,y,z}	0.077	0.077	-0.151	-0.226	-0.226	-0.287	-0.194	-0.194	-0.317	
M ^c	$\partial \mu_{x,y,z}$	-0.004	0.004	-0.004	0.986	0.986	0.986	0.940	0.940	0.940	

Table 9 Atomic polar tensors (e) in MeSiH₃, MeGeH₃, CH₄, SiH₄ and GeH₄

^az axis along CH or MH bond. These tensors are the transpose of those in the Gaussian output.

^bDiagonal elements only: others are zero. z axis along CM bond.

^cDiagonal elements only. z axis along the MH bond. DFT/6-311G** results.

MH bonds is well seen in the increases in the negative values of q, $d\mu/dr$ and μ from MH₄ to MeMH₃, the latter two combining to increase the unsigned χ .

The Mulliken charge q for the H(C) atom is slightly more positive in MeSiH₃ than it is in MeGeH₃, and significantly more so than in CH₄. In this way we can understand why the negative $d\mu/dr_{CH}$ becomes less so in the sequence $CH_4 - MeGeH_3 - MeSiH_3$. However, the bond moments μ_{CH} do not vary in a simple way, nor can the King effective charge χ be readily interpreted in a situation where $d\mu/dr$ and μ have opposite signs. In a number of situations where $d\mu/dr$ dr and μ for the CH bond vary, χ apparently tends to remain unchanged [42]. In the present molecules,

Table 10 Atomic charges and other properties for H atoms in silanes and germanes

Molecule	Method	Bond	q^{a}	χ ^b	\bar{P}^{c}	β^{d}	\bar{P}/β	$d\mu/dr^{e}$	ϕ^{i}
CH4	DFT	СН	0.109	0.108	0.002	0.228	0.004	-0.151	0
SiH ₄	DFT	SiH	-0.126	0.248	-0.247	0.061	-4.050	-0.287	0
GeH₄	DFT	GeH	-0.092	0.242	-0.235	0.124	-1.902	-0.318	0
MeSiH	DFT	CH	0.135	0.095	0.009	0.201	0.043	-0.118	9.64
MeSiH	SCF	CH	0.183	0.109	-0.003	0.231	-0.012	0.150	7.99
MeSiH	DFT	SiH	-0.139	0.280	-0.271	0.094	-2.941	-0.329	4.94
MeSiH	SCF	SiH	-0.150	0.353	-0.348	0.137	-2.547	~0.433	3.25
MeGeH	DFT	СН	0.127	0.092	-0.005	0.196	-0.026	-0.120	14.45
MeGeH	DFT	GeH	-0.103	0.276	-0.266	0.149	-1.783	-0.360	5.43

^aMulliken atomic charge (e).

^bKing effective atomic charge (e).

'Mean atomic dipole moment (e).

^dTensor anisotropy (e).

^eBond dipole derivative with respect to bond stretching (e).

¹Angle between $d\mu/dr$ and bond (°).

^gPermanent dipole moments: MeSiH₃, 0.7386 D; MeGeH₃, 0.7198 D; direction (+)H-C-M-H(-).

Molecule	Bond	n ^a	ΣA^{h}	$\sum A/n$	
CH1	СН	4	83.8	21.0	
MeSiH	СН	3	27.7	9.2	
MeGeH ;	СН	3	30.7	10.2	
SiH ₄	SiH	4	363.8	90.9	
MeSiH ;	SiH	3	359.9	120.0	
GeH	GeH	4	382.1	95.5	
MeGeH	GeH	3	374.2	124.7	

Table 11 Infra-red intensities A (km mol⁻¹) of CH and MH stretching vibrations, from DFT calculations

n =number of bonds.

^bTotal stretching intensity.

however, small changes are evident from the DFT results.

Variations in $d\mu/dr$ can be demonstrated more directly by observing the change in infra-red intensity per CH or MH bond, as shown in Table 11. The increase of SiH or GeH stretching intensity due to methyl substitution contrasts with the diminution calculated for the effect of a chlorine on the SiH bond [43].

Another feature to be noted in Table 10 is the extent to which $d\mu/dr$ departs from the direction of the bond, as measured by the angle ϕ . As might be expected from the charge undeformabilities, ϕ is markedly smaller for the SiH or GeH bond than it is for the CH one, and the deviation for the latter increases from methylsilane to methylgermane. This follows a pattern familiar in the methyl halides whereby the deviation increases in proportion to the polarisability of the X atom attached to the carbon [26].

To the extent that MH stretching involves only the

parameter $d\mu/dr$, and ignoring the small rotation of the permanent moment that has to occur in the antisymmetric stretching vibration, to conserve angular momentum, the ratio of the intensities of the antisymmetric and symmetric modes should be given by $\tan^2 \theta$ where θ is the angle between $d\mu/dr$ and the MC bond. On this assumption the QM calculated intensities should give directly a value for this angle, which may then be compared with the exact value from the rotated atomic polar tensor. The comparison of these two angles is shown in Table 12.

The agreement on the direction of $d\mu/dr$ is pleasingly close, which indicates the degree to which these motions may be regarded as purely stretching ones, involving only the CH or MH bond. As might be expected, the agreement improves as the weight of the atom to which the hydrogen is attached increases. Also of interest is the change in the A_{as}/A_{x} ratio that occurs between a DFT calculation and an

Table 12

Ratios of calculated antisymmetric and symmetric infra-red stretching intensities in relation to direction of $d\mu/dr$, for CH₃. SiH₃ and GeH₃ groups

Molecule	Bond/method	A ^a _{as}	A ^b _s	$A_{\rm s}/A_{\rm s}$	θ_{bond}^{z}	$\theta_{d\mu/dr}$ (pred) ^d	$\theta_{d\mu/dr}$ (apt) ^c
MeSiH :	CH/DFT	21.12	6.53	3.236	110,949	119.07	120.59
MeSiH ₃	CH/SCF	37.96	9.99	3.799	111.111	117.16	119.10
MeSiH ₃	SiH/DFT	291.44	68.47	4.256	110.658	115.86	115.60
MeSiH 3	SiH/SCF	513.88	102.23	5.027	110,602	114.04	113.85
MeGeH	CH/DFT	20.45	10.28	1.989	110.307	125.34	124.75
MeGeH	GeH/DFT	304.12	70.05	4.341	110.401	115.64	115.83

^aInfra-red intensity of asymmetric stretch (km mol⁻¹).

^bInfra-red intensity of symmetric stretch (km mol⁻¹).

^cAngle between bond and MC bond (°).

^dAngle between $d\mu/dr$ and MC bond (°), from $\theta = \tan^{-1}(A_{,p}/A_{,v})^{1/2}$.

^cAngle between $d\mu/dr$ and MC bond (°) from the atomic polar tensor.

SCF one. It is clear that this is almost wholly due small changes in the direction of $d\mu/dr$. The change in the ratio A_{as}/A_s from DFT to SCF is 1.174 for the CH bond and 1.181 for the SiH one, where the values predicted from $\theta_{d\mu/dr}$ (APT) are 1.143 and 1.174 respectively.

Clearly, care will be needed in deciding what level of theory is required in any attempt to divide infra-red intensity observed for a pair of overlapping bands between the transitions concerned.

6. Conclusions

For methylsilane and methylgermane a scaled triple- ζ DFT force field produces a good overall fit to all kinds of experimental data available. Strong evidence is obtained for the existence of already suspected Fermi resonances. A few off-diagonal constants require refining to achieve a better fit to the data, but the possibility that the latter are affected by unsuspected resonances cannot be ruled out at this stage. Both scaled and empirical force fields identify likely errors in the location of certain band centres. In general, high-resolution studies on these molecules are needed to enable a more rigorous test of theoretical predictions to be carried out.

Scale factors for various types of motion in the DFT force field cannot yet be predicted in advance and the widest possible variety of such factors should be employed if a good description of the vibrations is to be attained.

DFT-based atomic polar tensors, atomic charges and dipole derivatives illustrate principles previously found in experimental work on MH_4 molecules. There is a marked effect of methyl substitution in increasing MH stretching intensity, which is in keeping with its conventional inductive effect.

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