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Variational calculations of vibrational energy levels for XY_4 molecules
1. Stretching states

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A variational method for calculating excited stretching states of symmetric tetrahedral pentaatomic molecules is presented based on the use of Radau coordinates and Morse oscillator-like basis functions. Symmetry is used both to reduce the size of the secular matrix to be diagonalized and to calculate the potential energy matrix elements over a reduced grid of quadrature points. Test results are presented for methane, silane and germane. For CH_4, stretch–bend coupling is found to be significant, whereas it is less important for the more strongly local mode SiH_4 and GeH_4 molecules. Converged results are obtained for stretching states significantly higher than considered in previous calculations. These states will be used to represent stretching motions in a fully coupled stretch–bend calculation.

1. Introduction

The spectroscopy of the tetrahedral XY_4 molecules has been studied extensively. For a review of early work on XH_4 (X = C, Si, Ge, Sn, Pb) the reader is referred to Bürger and Bahner [1]. Probably the most important of these systems is methane. Methane is the third most important greenhouse gas, is present in many planetary atmospheres and is a major component of the atmosphere of cool stars, particularly the newly identified ultracool T stars. The way methane absorbs and emits light remains poorly understood, particularly when it is hot. A better theoretical understanding of the methane rovibrational spectrum would undoubtedly lead not only to more information being obtained from the astronomical spectra but also to better modelling of methane in many other situations. A bibliography on experimental work on methane spectra can be found in [2–5].

Some variational vibration–rotation calculations have already been performed for methane [3–6]. However these studies are tractable because they make approximations based on the molecule being semi-rigid or on the form of the potential energy surface, or both. It is unlikely that these approaches will be reliable for the highly excited states necessary to treat the hot methane problem.

Here we report on progress in developing a full variational treatment of the methane rotation–vibration problem. The procedure adopted is general to XY_4 type molecules and makes no assumption about any decoupling of modes in the potential energy hypersurface. This lack of decoupling implies full 9-dimensional quadrature over the potential. However, this cost is moderated by taking advantage of the symmetry inherent in these XY_4 systems, itself a subject of considerable study [7, 8]. When highly excited vibrational states of XY_4 systems are desired, the computation can easily suffer from basis set explosion: the number of product basis functions is of order N^F, where the number in each dimension N is of the order of 10 and F, the number of degrees of freedom, is 9. Using $N = 10$ to represent the desired states accurately then results in a total of 10^9 basis functions. Numerical quadrature suffers from similar problems of scaling.

Our strategy, besides taking the maximum advantage of symmetry, is to solve separate, reduced Hamiltonians for the stretches and the bends, and to use the results of these to solve the full coupled problem. So far we have developed a procedure for treating the stretching and bending motion of XY_4 molecules. For the non-rotating XY_4 systems, the vibrational motions can be divided into stretches (four coordinates) and bends (five independent coordinates). In this paper (part 1) we report results obtained using our stretch-only Hamiltonian; part 2 [9] presents results obtained for the bending prob-

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lem, including a discussion of the well known problem of redundancy in these coordinates.

2. Theory

2.1. *The Hamiltonian*

The exact vibrational Hamiltonian of XY_4 molecules can be expressed in terms of internal Radau coordinates. For XY_4 molecules, this is conveniently similar to the standard valence coordinates of the system. This form not only retains the symmetry of the methane problem but also gives a simple, orthogonal (i.e. diagonal in differential operators) kinetic energy operator. A method for constructing a vibrational Hamiltonian for an XY_4 system in Radau coordinates has been given by Schwenke [10] and Mladenovic [11]. Using their approach, the expression for the vibrational kinetic energy T_v of XY_4 in Radau coordinates, with X as the central atom, can be written as the sum of an angular contribution T_{ang} to the vibrational kinetic energy operator in the six angular coordinates α_{ij} and stretching kinetic energy T_{str}. Thus the $J = 0$ Hamiltonian is

$$H = T_{\mathrm{str}} + T_{\mathrm{ang}} + V, \tag{1}$$

with

$$T_{\mathrm{str}} = -\frac{\hbar^2}{2\mu}\sum_{i=1}^{4}\frac{\partial^2}{\partial r_i^2}, \tag{2}$$

and

$$\begin{aligned} T_{\mathrm{ang}} = & -\frac{\hbar^2}{2\mu}\sum_{i=1}^{3}\sum_{j>i}^{4}\left(\frac{1}{r_i^2}+\frac{1}{r_j^2}\right)\frac{\partial}{\sin\alpha_{ij}\partial\alpha_{ij}}\sin\alpha_{ij}\frac{\partial}{\partial\alpha_{ij}} \\ & -\frac{\hbar^2}{\mu}\sum_{i=1}^{4}\frac{1}{r_i^2}\sum_{j\neq i}^{4}\sum_{k\neq ij}^{4}\operatorname{csec}\alpha_{ij}\ \operatorname{csec}\alpha_{ik}(\cos\alpha_{jk} \\ & -\cos\alpha_{ij}\ \cos\alpha_{ik})\frac{\partial^2}{\partial\alpha_{ij}\partial\alpha_{ik}}. \end{aligned} \tag{3}$$

Here μ is the mass of atom Y, r_i is the Radau radial vector, and α_{ij} is the angle between the vector $\mathbf{r}_i$ and $\mathbf{r}_j$. In this work these angles are fixed at their equilibrium value, the tetrahedral angle, giving an effective stretching Hamiltonian. This eliminates T_{ang}; part 2 deals with the solution of the angular problem [9].

2.2. *Symmetry, basis functions and matrix elements*

For the radial problem, we evaluate the kinetic energy matrix elements for each of five possible total symmetry types, denoted in standard point group notation A_1, A_2, E, F_1, F_2. For a symmetrized basis set it is necessary to consider basis functions that satisfy the relationship $N \geq a \geq b \geq c \geq d$ where N denotes the highest quantum number in the basis and hence controls size of the basis set. Symmetrized functions arise from eight different basis types, which may be denoted

$$aaaa, abbb, aaad, aacc, abcc, abbd, aacd, abcd \tag{4}$$

For example, the wavefunction in case *abbb* with A_1 and F_2 symmetry types is

$$|abbb, \mathrm{A}_1\rangle = \frac{1}{2}(abbb + babb + bbab + bbba) \tag{5}$$

$$|abbb, \mathrm{F}_{2x}\rangle = \frac{1}{2}(abbb - babb + bbab - bbba) \tag{6}$$

$$|abbb, \mathrm{F}_{2y}\rangle = \frac{1}{2}(abbb - babb - bbab + bbba) \tag{7}$$

$$|abbb, \mathrm{F}_{2z}\rangle = \frac{1}{2}(abbb + babb - bbab - bbba) \tag{8}$$

General forms for these basis functions are given by Child and Halonen [12], who actually only consider 5 rather than the 8 classes used here. We have rederived the functions of Child and Halonen; our results agree with theirs with the exception of the $|abcd, \mathrm{F}_1\rangle$ functions, which we find to take the opposite sign. This phase difference is not significant in some case but matters for the method of computing the matrix elements over the potential (see later in equation (10)).

Symbolic kinetic energy matrix elements for these symmetrized basis functions were derived by hand and checked by using 'Mathematica'. In all cases the matrix elements can be reduced to simple sums over 1-dimensional integrals. These were then coded in Fortran 90.

2.3. *Potential matrix elements*

As we assume an arbitrary form for the stretching potential energy hypersurface, the integration must be done numerically, using quadrature, in 4 dimensions. Initially we took advantage of the symmetry of the basis function but not of the quadrature. The numerical evaluation of radial potential matrix elements is then given by

$$\begin{aligned} \langle abcd, \Gamma|V|a'b'c'd', \Gamma\rangle = & \sum_{\alpha=1}^{M}\sum_{\beta=1}^{M}\sum_{\gamma=1}^{M}\sum_{\delta=1}^{M}\omega_{\alpha\beta\gamma\delta} \\ & \times \Psi^{\Gamma}_{abcd}(\alpha\beta\gamma\delta)\Psi^{\Gamma}_{a'b'c'd'}(\alpha\beta\gamma\delta) \\ & \times V(\alpha\beta\gamma\delta), \end{aligned} \tag{9}$$

where $\alpha\beta\gamma\delta$ denote a point in four Mth-order (Gaussian) quadrature grids and $\omega_{\alpha\beta\gamma\delta}$ is the corresponding product of weights. This approach is demanding of both memory and CPU time. It is also inefficient, because it involves repeated evaluation of the potential at points related by symmetry.

Therefore we have derived formulae for symmetrized quadrature based on use of the reduced set of points

Table 1. Weighting factors for the possible combination of grid points with symmetry.

Case	Grid points	W
1	$\alpha\alpha\alpha\alpha$	1
2	$\alpha\beta\beta\beta$	4
3	$\alpha\alpha\alpha\delta$	4
4	$\alpha\alpha\gamma\gamma$	6
5	$\alpha\beta\gamma\gamma$	12
6	$\alpha\beta\beta\delta$	12
7	$\alpha\alpha\gamma\delta$	12
8	$\alpha\beta\gamma\delta$	24

Table 2. Optimized Morse parameters [15] of methane, silane and germane in atomic units.

Molecule	ω_e	r_e	D_e
CH_4	0.012 79	2.2298	0.0445
SiH_4	0.009 16	3.0988	0.1725
GeH_4	0.009 02	3.1624	0.1582

given by $M \geq \alpha \geq \beta \geq \gamma \geq \delta \geq 1$. This somewhat complicates the expression for the potential matrix elements as this symmetrization mixes different components (denoted Γ_i below) for degenerate representations. The new expression is:

$$\begin{aligned}\langle abcd, \Gamma | V | a'b'c'd', \Gamma \rangle = h^{-1} \sum_{\alpha=1}^{M} \sum_{\beta=1}^{\alpha} \sum_{\gamma=1}^{\beta} \sum_{\delta=1}^{\gamma} \omega'_{\alpha\beta\gamma\delta} \\ \times V(\alpha\beta\gamma\delta) \sum_{i=1}^{h} \Psi_{abcd}^{\Gamma_i}(\alpha\beta\gamma\delta) \\ \times \Psi_{a'b'c'd'}^{\Gamma_i}(\alpha\beta\gamma\delta), \qquad (10)\end{aligned}$$

where h is the degree of degeneracy; $h = 1, 2, 3$ for A, E and F representations, respectively.

Our new formulation requires only the potential evaluations at unique points. The weight $\omega'_{\alpha\beta\gamma\delta}$ in equation (10) is related to the standards weights $\chi_{\alpha\beta\gamma\delta}$ in equation (9) by a factor that depends on the number of unique geometries there are for the particular combination of grid points. Again there are eight possible cases, which are listed in Table 1 along with their extra weighting, W. The new weight is then given by

$$\omega'_{\alpha\beta\gamma\delta} = W\omega_{\alpha\beta\gamma\delta}. \qquad (11)$$

The new algorithm is not only more efficient in computer time, since it significantly reduces the number of potential evaluations, but also it uses much less memory. This is because our algorithm involves storing the wavefunctions in memory at each integration point, thus reducing the number of points saved in memory. In practice the new algorithm is some 5–20 times quicker than the old one, depending on the details of the problem under investigation, and reduces the overall memory requirement by a factor of more than 20.

2.4. *Computational details*

The radial motions were represented using a basis of Morse oscillator-like functions of Tennyson and Sutcliffe [13]. These Laguerre polynomial functions, which are adapted from standard Morse functions to provide a complete set, have proved very successful for triatomic species [14]. In this scheme, the basis functions are parametrized using the Morse parameters ω_e, r_e, D_e [15], which may be variationally optimized for each system under investigation. Table 2 presents the parameters optimized for the systems considered here.

Table 3. Vibrational band origins (in cm^{-1}) for the Ith stretching state of methane with A_1 symmetry as function of basis set size.

	E_{26}	$E_{24}-E_{26}$	$E_{21}-E_{24}$	$E_{18}-E_{21}$	$E_{15}-E_{18}$
$1 = 1$	2 918.42	0.00	0.00	0.00	0.00
2	5 798.85	0.00	0.00	0.00	0.00
3	6 035.95	0.00	0.00	0.00	0.00
5	8 625.64	0.00	0.00	0.00	0.01
6	8 796.00	0.00	0.00	0.00	0.01
7	9 084.07	0.00	0.00	0.00	0.00
8	11 345.11	0.00	0.01	0.09	0.63
9	11 533.06	0.00	0.00	0.03	0.25
10	11 808.71	0.00	0.00	0.01	0.11
11	11 933.59	0.00	0.00	0.00	0.01
21	17 106.59	0.03	0.13	0.35	4.51
27	18 700.82	10.69	64.16	202.74	320.62
28	19 311.59	1.29	9.71	71.06	288.68
29	19 704.65	0.11	0.86	9.69	182.65
31	19 929.84	0.12	0.48	1.32	13.36
38	20 874.50	0.00	0.01	0.09	0.73

Table 4. Vibrational band origins (in cm^{-1}) for the Ith stretching state of germane with A$_1$ symmetry as a function of basis set size.

	E_{26}	$E_{24}-E_{26}$	$E_{21}-E_{24}$	$E_{18}-E_{21}$	$E_{15}-E_{18}$
$I = 1$	2 110.77	0.00	0.00	0.00	0.00
2	4 153.51	0.00	0.00	0.00	0.00
3	4 221.96	0.00	0.00	0.00	0.00
4	6 127.71	0.00	0.00	0.00	0.00
5	6 264.83	0.00	0.00	0.00	0.01
6	6 333.56	0.00	0.00	0.00	0.01
7	8 033.53	0.00	0.00	0.00	0.00
8	8 239.43	0.00	0.00	0.00	0.04
9	8 308.22	0.00	0.00	0.00	0.03
10	8 376.57	0.00	0.00	0.00	0.11
11	8 445.59	0.00	0.00	0.00	0.02
21	12 258.00	0.00	0.00	0.00	0.10
26	13 340.74	0.01	0.17	1.92	19.38
27	13 752.66	0.00	0.01	0.28	6.00
28	14 027.48	0.00	0.00	0.01	1.09
29	14 096.04	0.00	0.00	0.02	2.02
31	14 164.65	0.00	0.00	0.00	1.00
38	14 973.37	0.32	4.06	25.86	121.99
41	15 865.71	0.00	0.04	0.76	18.30
51	16 543.82	4.91	3.32	0.32	38.17
52	16 552.05	0.00	37.18	32.08	12.31
53	16 621.27	0.00	0.00	105.22	321.95
60	17 979.18	0.00	0.05	1.15	43.77

Table 5. Band origins (in cm^{-1}) of the stretching vibrational states of methane. For the observed band origins, the results are given as observed − calculated.

		Halonen [6]		Schwenke and Partridge [3]	
	Observed	From [6]	This work	From [3]	This work
1000A$_1$	2 916.48 [5]	1.85	−1.94	2.71	−14.54
1000F$_2$	3 019.49 [5]	−1.60	−39.72	5.29	−20.28
2000A$_1$	5 790.25 [5]	−0.69	−8.59	−3.95	−30.75
2000F$_2$	6 004.60 [5]	−3.30	−36.22	8.40	−26.88
3000A$_1$			8 625.63		8 633
3000F$_2$	8 807 [2]		−64		−52
4000A$_1$			11 345		11 271
4000F$_2$	11 277 [2]		−77		3
5000A$_1$			13 919		13 666
5000F$_2$	13 755 [2]		−165		88
6000A$_1$			16 368		16 643
6000F$_2$	16 155 [2]		−213		−489
7000A$_1$			18 700		18 843
7000F$_2$	18 420 [2]		−291		−423
8000A$_1$			21 082		21 261
8000F$_2$	20 600 [2]		−620		−609

Numerical integration over the potential was performed using Gauss–Laguerre quadrature based on the definition of the Morse-like functions. Previous work [13] has shown that $M = N + 3$ grid points are sufficient for reliable quadrature, where N is the order of the basis functions in that dimension. This finding was confirmed by the present study, and all the results presented below used this number of quadrature points.

3. Results

3.1. *Basis set convergence*

For testing purposes we used the local mode, valence coordinate potential function of Halonen and Child [12]. Tables 3 and 4 show the convergence of our calculations with increasing basis set size for A_1 symmetry calculations on methane and germane, respectively. Other symmetries show similar convergence characteristics. Silane, considered further below, was found to be intermediate between the other two systems.

The tables show that, for most of the states considered, excellent convergence with respect to increasing basis set size is achieved for $N = 26$, which implies a matrix of size 1683 for A_1 symmetry. However, there are a few states that show markedly slower convergence than the others. Analysis showed that these states were the pure local modes (see Jensen [16]) and have the general assignment (n000, A_1).

For example, use of $N = 18$ converges the (6000, A_1) local mode state to within 0.06 cm^{-1} for germane, 0.67 cm^{-1} for silane and 9.28 cm^{-1} for methane. Increasing N to 24 converges these states but only converges the (8000, A_1) local mode state to 0.32 cm^{-1} for germane,

Table 6. Band origins (in cm^{-1}) of the stretching states of silane. For the observed band origins, the results are given as observed − calculated.

		Model 1 [12]		[24]	Model 2 [12]	
	Observed	From [12]	This work	This work	From [12]	This work
$1000A_1$	2 186.87 [17]	0.07	0.01	0.31	0.27	0.18
$000F_2$	2 189.19 [17]	0.89	1.95	1.18	0.39	1.43
$2000A_1$	4 308.87 [21]	1.07	2.57	1.23	−0.23	1.23
$2000F_2$	4 309.35 [21]	0.45	1.91	1.61	0.15	1.65
$1100A_1$	4 374.56 [24]	−1.34	−0.95	−0.04	−0.54	−0.11
$1100F_2$	4 378.40 [24]	0.90	2.41	2.35	1.10	2.66
1100E	4 380.28 [24]	1.88	4.03	3.51	1.88	4.00
$3000A_1$	6 362.05 [20]	−0.15	2.04	1.83	−0.65	1.45
$3000F_2$	6 362.05 [20]	−0.15	2.01	1.82	−0.65	1.45
$2100F_2$	6 496.13 [22]	−2.47	0.08	0.16	−1.47	0.10
$2100F_1$	6 497.45 [22]	−1.95	0.51	−0.48	0.75	−0.03
$2100A_1$	6 500.30 [24]	0.30	2.08	4.91	−0.30	4.69
$2100F_2$	6 500.60 [24]	−0.20	1.52	3.25	0.80	3.56
2100E	6 502.88 [24]	1.38	3.64	6.32	4.48	6.41
$4000A_1$	8 347.86 [20]	−0.74	2.09	2.70	−1.14	1.64
$4000F_2$	8 347.86 [20]	−0.74	2.09	2.69	−1.14	1.64
$3100A_1$		8533.70	8551.17	8549.30	8552.10	8549.74
$3100F_2$	8 551.88 [23]	−2.42	0.39	2.50	−0.32	2.08
3100E		8555.00	8551.70	8550.41	8553.70	8550.57
$3100F_1$	8 553.50 [23]	−2.60	0.34	3.04	−0.30	2.90
$5000A_1$	10 266.49 [17]	−1.31	2.12	3.94	−1.41	1.94
$5000F_2$	10 266.49 [17]	−1.31	2.12	3.94	−1.41	1.93
$4100A_1$	10 542.70 [24]	0.00	3.05	7.67	3.60	6.56
$4100F_2$	10 542.70 [24]	−0.10	3.06	7.66	3.60	6.55
$6000A_1$	12 120.00 [23]	0.20	4.17	7.34	0.60	4.41
$6000F_2$	12 120.00 [23]	0.20	4.17	7.34	0.60	4.41
$7000A_1$	13 900.40 [24]	−4.20	0.26	−1.96	−3.20	0.43
$7000F_2$	13 900.40 [24]	−4.20	0.26	−1.96	−3.20	0.43
$8000A_1$	15 625.40 [24]	3.20	7.94		5.40	9.45
$8000F_2$	15 625.40 [24]	3.20	7.94		5.40	9.45
$9000A_1$	17 266.60 [24]	−6.00	−4.53		−4.00	−1.93
$9000F_2$	17 266.60 [24]	−6.00	−4.53		−4.10	−1.93

0.11 cm^{-1} for silane and a very poor 137.79 cm^{-1} for methane. For all lower states, the $N = 24$ basis converges the energies to within 0.1 cm^{-1}. Therefore the calculations reported below were performed using the $N = 24$ basis. This gives final matrices of dimensions 1298, 515, 1690, 2163 and 2933 for A_1, A_2, E, F_1 and F_2 symmetries, respectively. The notation E_N stands for the energy obtained from a basis set with up to N 1-dimensional stretching basis functions and $N + 3$ quadrature points.

3.2. *Comparison with experiment*

Calculations were performed using a number of potentials for methane, silane and germane. The results of these calculations were compared with previous studies and known experimental band origins. These results are presented in tables 5–8. For nearly all the states our results are stable to better than 0.01 cm^{-1} with respect to increasing the basis. A full set of calculated vibrational band origins for each system, covering all 5 symmetries, has been placed in the journal archive.

For methane, we used the *ab initio* stretching potential functions of Schwenke and Partridge [3] and the empirically determined one of Halonen [6]. Results for the band origins are given in table 5. The table also compares the data with results given in the works cited, both of which consider only relatively low levels of excitation.

The source of the differences between our calculations and previous ones is somewhat different in origin. Halonen [6] employed a second-order perturbation theory expansion and a spectroscopic model. His third-order force constant expansion, which we employ here, is thus not exactly the same potential as the one implied by his model. Conversely, Schwenke and Partridge [3] performed full coupled stretch–bend calculations, albeit over a limited energy range. Differences from their results thus give a measure of the importance of stretch–bend coupling in determining the band origins of the stretching states. The importance of these stretch–bend coupling effects for methane means that little is to be gained from a direct comparison of our results with the experimental data. However, our method is capable of getting converged results over the entire range of energies for which experimental data are available, which extends to over 20 000 cm^{-1}. This suggests that with the inclusion of stretch–bend coupling

Table 7. Band origins (in cm^{-1}) of the stretching vibrational states of $^{70}\text{GeH}_4$. For the observed band origins, the results are given as observed − calculated.

		PES 1 [12]	PES 2 [12]	Zhu *et al.* [27]	
	Observed	This work	This work	From [27]	This work
$1000A_1$	2 110.72 [26]	−0.04	−0.04	0.14	0.14
$1000F_2$	2 112.03 [26]	0.01	−0.00	0.37	0.56
$2000A_1$	4 154.80 [27]	0.05	−0.15	0.18	0.46
$2000F_2$	4 155.12 [27]	0.10	0.12	0.03	0.31
$1100A_1$		4 222.82	4 222.47		4 222.28
$1100F_2$		4 224.10	4 223.73		4 223.19
$3000A_1$	6 130.45 [27]	0.28	0.60	−0.28	0.13
$3000F_2$	6 130.45 [28]	0.26	0.60	−0.31	0.11
$2100F_2$		6 267.30	6 266.02		6 266.83
$2100A_1$	6 265.20 [23]	−2.41	−1.33		−1.59
$4000A_1$		8 036.95	8 036.28		8 038.17
$4000F_2$		8 036.95	8 036.27		8 038.17
$3100A_1$		8 243.00	8 241.78		8 242.91
$3100F_2$		8 243.36	8 241.83		8 243.22
$5000A_1$	9 878.60 [29]	3.19	4.31		0.40
$5000F_2$	9 878.60 [29]	3.20	4.31		0.40
$4100A_1$		10 150.85	10 148.55		10 151.84
$4100F_2$		10 150.85	10 148.55		10 151.84
$6000A_1$	11 650.33 [25]	4.48	6.46	−0.84	−0.10
$6000F_2$	11 650.33 [25]	4.78	6.46	−0.84	−0.10
$7000A_1$	13 356.06 [25]	8.49	10.86	−0.22	1.18
$7000F_2$	13 356.06 [25]	8.49	10.86	−0.22	1.18
$8000A_1$		14 985.66	14 982.78		14 992.09
$8000F_2$	14 996.41 [25]	10.75	13.63	2.76	4.32

this procedure should be capable of addressing problems that cannot be tackled by other variational approaches.

For silane, calculations were performed using two spectroscopically determined potentials due to Halonen and Child [12] (table 6). Comparison is made with the more approximate stretch-only calculations of Halonen and Child, and of Wang and Silbert [24]. Unlike methane, the various approximate treatments all give results in reasonable agreement both with the experimental measurements [17–22] and each other. All the results generally agree within 2 cm^{-1} for the lower states and 5 cm^{-1} for the higher ones. Silane is a much stronger local mode system than methane. It would appear that for silane not only is stretch–bend coupling greatly reduced but also the stretching motion can be treated to reasonable accuracy using methods based on approximate expansions.

The vibrations of germane have a very strongly local mode character, and therefore one would anticipate that this system should also be amenable to a stretch-only treatment. Our calculations were performed using the two model potential energy surfaces (denoted PES (1) and (2)) due to Halonen and Child [12], and gave results in good agreement with those of Halonen and Child (not given) and with the experimental band origins [25, 27–29] (see tables 7 and 8). For lower states our calculations reproduce experiment to within 1 cm^{-1}, although this increases to 5 cm^{-1} for higher stretching states.

We also performed calculations using the more recent potential energy surface of Zhu *et al.* [27], whose fitted

Table 8. Band origins (in cm^{-1}) of the stretching vibrational states of $^{74}\mathrm{GeH}_4$ and $^{74}\mathrm{GeD}_4$. For the observed band origins, the results are given as observed − calculated.

		PES 1 [12]	PES 2 [12]	Zhu *et al.* [27]	
	Observed	This work	This work	From [27]	This work
$^{74}\mathrm{GeH}_4$					
1000A_1	2 110.70 [26]	−0.07	−0.07	0.11	0.11
1000F_2	2 111.14 [26]	0.15	0.14	0.52	0.70
2000A_1	4 153.57 [27]	0.28	0.07	0.44	0.69
2000F_2	4 153.82 [27]	0.09	0.30	0.26	0.50
1100A_1		4 222.33	4 221.96		4 221.79
1100F_2	4 222.70 [23]	0.14	0.51		1.04
3000A_1	6 128.60 [27]	0.53	0.89	0.06	0.43
3000F_2	6 128.60 [27]	0.56	0.89	0.04	0.42
2100F_2	6 263.70 [29]	−1.59	−1.44		−2.09
2100A_1		6 266.09	6 264.83		6 265.60
4000A_1	8 034.40 [23]	0.22	0.87		−0.99
4000F_2	8 034.40 [23]	0.22	0.87		−1.00
3100A_1	8 241.00 [23]	0.38	1.57		0.49
3100F_2	8 241.06 [23]	0.31	1.63		0.60
2200A_1		8 309.66	8 308.22		8 308.88
2200F_2	8 310.30 [29]	0.21	2.07		0.98
2110F_2	8 378.60 [29]	0.27	1.89		−0.33
2110A_1	8 380.10 [23]	0.44	3.27		3.08
5000A_1	9 875.78 [29]	3.71	4.81		0.92
5000F_2	9 875.78 [29]	3.71	4.81		0.92
4100A_1	10 148.10 [25]	0.26	2.55		−0.71
4100F_2	10 148.10 [25]	0.24	2.55		−0.73
6000A_1	11 647.23 [25]	5.53	7.19	−0.02	0.66
6000F_2	11 647.23 [25]	5.53	7.19	−0.02	0.66
7000A_1	13 352.66 [25]	9.57	11.91	0.82	2.10
7000F_2	13 352.66 [25]	9.57	11.91	0.82	2.10
8000A_1		14 976.84	13 973.69		14 987.35
800F_2		14 976.84	14 973.69		14 987.35
$^{74}\mathrm{GeD}_4$					
1000A_1	1 509.40 [29]	2.30	2.11	2.68	
1000F_2	1 522.70 [29]	2.30	2.10	2.68	
2000F_2	3 003.52 [29]	5.41	5.31	5.71	

potential gives results in almost perfect agreement with their related experimental studies [23, 29] (tables 7 and 8). Our calculations generally support the calculations of Zhu *et al*., who used a more approximate perturbative treatment. However, we show that although the potential remains good, it is less exact for vibrational band origins not considered in the study.

4. Conclusion

We have developed a general variational method for treating the stretch-only vibrational motions of XY_4 systems. Of particular important is our procedure for computing matrix elements over the potential energy surface by considering only the unique points on the surface.

Test calculations performed on methane, silane and germane in each case extend very considerably the range of stretching states for which converged results have been obtained. A comparison of our results with previous low energy studies suggests that the strength of stretch–bend coupling in methane makes stretch-only calculations unreliable. Conversely, the stretches of silane and germane, which are strongly local-mode in character, appear to be well represented by our stretch-only procedure.

The development of a stretch-only method for XY_4 systems represents a first step in our project to develop a general variational method for treating all 9 vibrational degrees of freedom in these systems at high levels of excitation. The second step in this project, the solution of the 5-dimensional bend-only problem, is discussed in paper 2.

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