Variational calculations of vibrational energy levels for XY_4 molecules: I stretching states.

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Abstract

A variational method for calculating excited stretching states of symmetric tetrahedral penta-atomic molecules is presented based on the use of Radau coordinates and Morse oscillator-like basis functions. Symmetry is used both to reduces the size of secular matrix to be diagonalized and to calculate 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

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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 ultra-cool 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 modeling of methane in many other situations. A bibliography on experimental work on methane spectra can be found in reference [2, 3, 4, 5].

Some variational vibration-rotation calculation have already been performed for methane [3, 4, 5, 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 which makes no assumption about any decoupling of modes in the potential energy hypersurface. This lack of decoupling implies full nine-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 order of N^F, where the number in each dimension, N, is on the order of 10 and F, the number of degrees of freedom, is 9. Using $N = 10$ to accurately represent the desired states then the 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 we report results obtained using our stretch-only Hamiltonian; the following paper [9] we present results obtained for the bending problem 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 standard valence coordinates of the system. This form not only retains the symmetry of the methane problem, but also gives a simple, orthogonal (ie 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 these approaches, 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

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

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

and

$$T_{ang} = -\frac{\hbar^2}{2\mu}\sum_{i=1}^{3}\sum_{j>i}^{4}(\frac{1}{r_i^2}+\frac{1}{r_j^2})\frac{\partial}{\sin\alpha_{ij}\partial\alpha_{ij}}\sin\alpha_{ij}\frac{\partial}{\partial\alpha_{ij}}$$

$$-\frac{\hbar^2}{\mu}\sum_{i=1}^{4}\frac{1}{r_i^2}\sum_{j\neq i}^{4}\sum_{k\neq ij}^{4}\csc\alpha_{ij}\csc\alpha_{ik}(\cos\alpha_{jk}-\cos\alpha_{ij}\cos\alpha_{ik})\frac{\partial^2}{\partial\alpha_{ij}\partial\alpha_{ik}} \tag{3}$$

where μ is the mass of atom Y, r_i is the Radau radial vector, and α_{ij} is the angle between the vector $\underline{r}_i$ and $\underline{r}_j$. In this work these angles are fixed at their equilibrium value, the tetrahedral angle, giving an effective stretching

Hamiltonian. This eliminates T_{ang}; the following paper deals with 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 which 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 can 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

$$|abbb, A_1 >= \frac{1}{2}(abbb + babb + bbab + bbba) \tag{5}$$

$$|abbb, F_{2x} >= \frac{1}{2}(abbb - babb + bbab - bbba) \tag{6}$$

$$|abbb, F_{2y} >= \frac{1}{2}(abbb - babb - bbab + bbba) \tag{7}$$

$$|abbb, F_{2z} >= \frac{1}{2}(abbb + babb - bbab - bbba) \tag{8}$$

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 $|abcd, F_1 >$ functions which we find to take the opposite sign. This phase difference is not significant in some case but matters for method of computing the matrix elements over the potential, see eq. (10) below.

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 one-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 four 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

$$< abcd,\Gamma|V|a'b'c'd',\Gamma >= \sum_{\alpha=1}^{M}\sum_{\beta=1}^{M}\sum_{\gamma=1}^{M}\sum_{\delta=1}^{M}\omega_{\alpha\beta\gamma\delta}\Psi^{\Gamma}_{abcd}(\alpha\beta\gamma\delta)\Psi^{\Gamma}_{a'b'c'd'}(\alpha\beta\gamma\delta)V(\alpha\beta\gamma\delta) \tag{9}$$

where $\alpha\beta\gamma\delta$ denote a point in four M^{th}-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 as it involves repeat evaluation of the potential at points related by symmetry.

We have therefore derived formulae for symmetrized quadrature based on use of the reduced set of points 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

Table 1: Weighting factor for the possible combination of grid point 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

degenerate representations. The new expression is:

$$< abcd, \Gamma|V|a'b'c'd', \Gamma >= h^{-1} \sum_{\alpha=1}^{M} \sum_{\beta=1}^{\alpha} \sum_{\gamma=1}^{\beta} \sum_{\delta=1}^{\gamma} \omega'_{\alpha\beta\gamma\delta} V(\alpha\beta\gamma\delta) \sum_{i=1}^{h} \Psi^{\Gamma_i}_{abcd}(\alpha\beta\gamma\delta) \Psi^{\Gamma_i}_{a'b'c'd'}(\alpha\beta\gamma\delta), \tag{10}$$

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

Our new formulation only requires the potential evaluations at unique points. The weight $\omega'_{\alpha\beta\gamma\delta}$ in eq (10) is related to the standards weights $\omega_{\alpha\beta\gamma\delta}$ in eq (9) by a factor which 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

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

The new algorithm is not only more efficient in computer time, since it sig-

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

Molecule	ω_e	r_e	D_e
CH_4	0.01279	2.2298	0.0445
SiH_4	0.00916	3.0988	0.1725
GeH_4	0.00902	3.1624	0.1582

nificantly reduces the number of potential evaluations, it also 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 saves memory. In practice the new algorithm is some 5 to 20 times quicker than the old one, depending on the details of the problem under investigation, and reduces the overall memory requirement by more than a factor of 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 parameterized using the Morse parameter ω_e, r_e, D_e [15] which can be variationally optimized for each system under investigation. Table 2 presents the parameters optimized for the systems considered here.

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 a quadrature, where N is the order of the basis functions in that dimension. This finding was confirmed by this study and all 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 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 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 which 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 converge 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, 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}. Calculations reported below were therefore performed using the $N = 24$ basis. This gives final

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

	E_{26}	$E_{24} - E_{26}$	$E_{21} - E_{24}$	$E_{18} - E_{21}$	$E_{15} - E_{18}$
I=1	2918.42	0.00	0.00	0.00	0.00
2	5798.85	0.00	0.00	0.00	0.00
3	6035.95	0.00	0.00	0.00	0.00
5	8625.64	0.00	0.00	0.00	0.01
6	8796.00	0.00	0.00	0.00	0.01
7	9084.07	0.00	0.00	0.00	0.00
8	11345.11	0.00	0.01	0.09	0.63
9	11533.06	0.00	0.00	0.03	0.25
10	11808.71	0.00	0.00	0.01	0.11
11	11933.59	0.00	0.00	0.00	0.01
21	17106.59	0.03	0.13	0.35	4.51
27	18700.82	10.69	64.16	202.74	320.62
28	19311.59	1.29	9.71	71.06	288.68
29	19704.65	0.11	0.86	9.69	182.65
31	19929.84	0.12	0.48	1.32	13.36
38	20874.50	0.00	0.01	0.09	0.73

matrices of dimension 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 one-dimensional stretching basis function 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

Table 4: Vibrational band origins, in cm^{-1}, for the I$^{\text{th}}$ stretching state of germane with A$_1$ symmetry as function of basis set size.

	E_{26}	$E_{24}-E_{26}$	$E_{21}-E_{24}$	$E_{18}-E_{21}$	$E_{15}-E_{18}$
I=1	2110.77	0.00	0.00	0.00	0.00
2	4153.51	0.00	0.00	0.00	0.00
3	4221.96	0.00	0.00	0.00	0.00
4	6127.71	0.00	0.00	0.00	0.00
5	6264.83	0.00	0.00	0.00	0.01
6	6333.56	0.00	0.00	0.00	0.01
7	8033.53	0.00	0.00	0.00	0.00
8	8239.43	0.00	0.00	0.00	0.04
9	8308.22	0.00	0.00	0.00	0.03
10	8376.57	0.00	0.00	0.00	0.11
11	8445.59	0.00	0.00	0.00	0.02
21	12258.00	0.00	0.00	0.00	0.10
26	13340.74	0.01	0.17	1.92	19.38
27	13752.66	0.00	0.01	0.28	6.00
28	14027.48	0.00	0.00	0.01	1.09
29	14096.04	0.00	0.00	0.02	2.02
31	14164.65	0.00	0.00	0.00	1.00
38	14973.37	0.32	4.06	25.86	121.99
41	15865.71	0.00	0.04	0.76	18.30
51	16543.82	4.91	3.32	0.32	38.17
52	16552.05	0.00	37.18	32.08	12.31
53	16621.27	0.00	0.00	105.22	321.95
60	17979.18	0.00	0.05	1.15	43.77

tables 5 – 7. For nearly all 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 with results given in the cited works, both of which only consider 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 with their results thus gives a measure of the importance of stretch-bend coupling 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 to 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 this procedure should be capable of addressing problems which cannot be tackled by other variational approaches.

For silane, calculations were performed using two spectroscopically determined potentials due to Halonen and Child [12], see 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 both in reasonable agreement with the experimental measurements [17, 18, 19, 20, 21, 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 that 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, one would therefore anticipate that this system should also be amenable to a stretch-only treatment. Our calculations performed using the two model potential energy surfaces (denoted PES (1) and (2)) due to Halonen and Child [12]. Calculations using this surface gave results in good agreement with those of Halonen and Child (not given) and with the experimental band origins [25, 27, 28, 29], see Table 7. For lower states our calculations reproduce experiment to within 1 cm^{-1}, although this increases to 5 cm^{-1} for higher stretching states.

We have also performed calculations using the more recent potential energy surface of Zhu *et al.* [27], whose fitted potential gives results in almost perfect agreement with their related experimental studies [23, 29]. Our calculations generally support the calculations of Zhu *et al.*, who used a more approximate perturbative treatment. However we show that while potential remains good, it is less exact for vibrational band origins not considered in the study.

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

	observed	Halonen [6]		Schwenke and Partridge [3]	
		[6]	this work	[3]	this work
$1000A_1$	2916.48 [5]	1.85	−1.94	2.71	−14.54
$1000F_2$	3019.49 [5]	−1.60	−39.72	5.29	−20.28
$2000A_1$	5790.25 [5]	−0.69	−8.59	−3.95	−30.75
$2000F_2$	6004.60 [5]	−3.30	−36.22	8.40	−26.88
$3000A_1$			8625.63		8633
$3000F_2$	8807 [2]		−64		−52
$4000A_1$			11345		11271
$4000F_2$	11277 [2]		−77		3
$5000A_1$			13919		13666
$5000F_2$	13755 [2]		−165		88
$6000A_1$			16368		16643
$6000F_2$	16155 [2]		−213		−489
$7000A_1$			18700		18843
$7000F_2$	18420 [2]		−291		−423
$8000A_1$			21082		21261
$8000F_2$	20600 [2]		−620		−609

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

	observed	Model 1 [12]		[24]	Model 2 [12]	
		[12]	this work	this work	[12]	this work
$1000A_1$	2186.87 [17]	0.07	0.01	0.31	0.27	0.18
$1000F_2$	2189.19 [17]	0.89	1.95	1.18	0.39	1.43
$2000A_1$	4308.87 [21]	1.07	2.57	1.23	−0.23	1.23
$2000F_2$	4309.35 [21]	0.45	1.91	1.61	0.15	1.65
$1100A_1$	4374.56 [24]	−1.34	−0.95	−0.04	−0.54	−0.11
$1100F_2$	4378.40 [24]	0.90	2.41	2.35	1.10	2.66
$1100E$	4380.28 [24]	1.88	4.03	3.51	1.88	4.00
$3000A_1$	6362.05 [20]	−0.15	2.04	1.83	−0.65	1.45
$3000F_2$	6362.05 [20]	−0.15	2.01	1.82	−0.65	1.45
$2100F_2$	6496.13 [22]	−2.47	0.08	0.16	−1.47	0.10
$2100F_1$	6497.45 [22]	−1.95	0.51	−0.48	0.75	−0.03
$2100A_1$	6500.30 [24]	0.30	2.08	4.91	−0.30	4.69
$2100F_2$	6500.60 [24]	−0.20	1.52	3.25	0.80	3.56
$2100E$	6502.88 [24]	1.38	3.64	6.32	4.48	6.41
$4000A_1$	8347.86 [20]	−0.74	2.09	2.70	−1.14	1.64
$4000F_2$	8347.86 [20]	−0.74	2.09	2.69	−1.14	1.64
$3100A_1$		8533.70	8551.17	8549.30	8552.10	8549.74
$3100F_2$	8551.88 [23]	−2.42	0.39	2.50	−0.32	2.08
$3100E$		8555.00	8551.70	8550.41	8553.70	8550.57
$3100F_1$	8553.50 [23]	−2.60	0.34	3.04	−0.30	2.90
$5000A_1$	10266.49 [17]	−1.31	2.12	3.94	−1.41	1.94
$5000F_2$	10266.49 [17]	−1.31	2.12	3.94	−1.41	1.93
$4100A_1$	10542.70 [24]	0.00	3.05	7.67	3.60	6.56
$4100F_2$	10542.70 [24]	−0.10	3.06	7.66	3.60	6.55
$6000A_1$	12120.00 [23]	0.20	4.17	7.34	0.60	4.41
$6000F_2$	12120.00 [23]	0.20	4.17	7.34	0.60	4.41
$7000A_1$	13900.40 [24]	−4.20	0.26	−1.96	−3.20	0.43
$7000F_2$	13900.40 [24]	−4.20	0.26	−1.96	−3.20	0.43
$8000A_1$	15625.40 [24]	3.20	7.94		5.40	9.45
$8000F_2$	15625.40 [24]	3.20	7.94		5.40	9.45
$9000A_1$	17266.60 [24]	−6.00	−4.53		−4.00	−1.93
$9000F_2$	17266.60 [24]	−6.00	−4.53		−4.10	−1.93

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

	observed	PES 1 [12]	PES 2 [12]	Zhu *et al.* [27]	
		this work	this work	[27]	this work
$1000A_1$	2110.72 [26]	-0.04	-0.04	0.14	0.14
$1000F_2$	2112.03 [26]	0.01	-0.00	0.37	0.56
$2000A_1$	4154.80 [27]	0.05	-0.15	0.18	0.46
$2000F_2$	4155.12 [27]	0.10	0.12	0.03	0.31
$1100A_1$		4222.82	4222.47		4222.28
$1100F_2$		4224.10	4223.73		4223.19
$3000A_1$	6130.45 [27]	0.28	0.60	-0.28	0.13
$3000F_2$	6130.45 [28]	0.26	0.60	-0.31	0.11
$2100F_2$		6267.30	6266.02		6266.83
$2100A_1$	6265.20 [23]	-2.41	-1.33		-1.59
$4000A_1$		8036.95	8036.28		8038.17
$4000F_2$		8036.95	8036.27		8038.17
$3100A_1$		8243.00	8241.78		8242.91
$3100F_2$		8243.36	8241.83		8243.22
$5000A_1$	9878.60 [29]	3.19	4.31		0.40
$5000F_2$	9878.60 [29]	3.20	4.31		0.40
$4100A_1$		10150.85	10148.55		10151.84
$4100F_2$		10150.85	10148.55		10151.84
$6000A_1$	11650.33 [25]	4.48	6.46	-0.84	-0.10
$6000F_2$	11650.33 [25]	4.78	6.46	-0.84	-0.10
$7000A_1$	13356.06 [25]	8.49	10.86	-0.22	1.18
$7000F_2$	13356.06 [25]	8.49	10.86	-0.22	1.18
$8000A_1$		14985.66	14982.78		14992.09
$8000F_2$	14996.41 [25]	10.75	13.63	2.76	4.32

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

	observed	PES 1 [12]	PES 2 [12]	Zhu *et al.* [27]	
		this work	this work	[27]	this work
$^{74}\mathrm{GeH}_4$					
$1000A_1$	2110.70 [26]	-0.07	-0.07	0.11	0.11
$1000F_2$	2111.14 [26]	0.15	0.14	0.52	0.70
$2000A_1$	4153.57 [27]	0.28	0.07	0.44	0.69
$2000F_2$	4153.82 [27]	0.09	0.30	0.26	0.50
$1100A_1$		4222.33	4221.96		4221.79
$1100F_2$	4222.70 [23]	0.14	0.51		1.04
$3000A_1$	6128.60 [27]	0.53	0.89	0.06	0.43
$3000F_2$	6128.60 [27]	0.56	0.89	0.04	0.42
$2100F_2$	6263.70 [29]	-1.59	-1.44		-2.09
$2100A_1$		6266.09	6264.83		6265.60
$4000A_1$	8034.40 [23]	0.22	0.87		-0.99
$4000F_2$	8034.40 [23]	0.22	0.87		-1.00
$3100A_1$	8241.00 [23]	0.38	1.57		0.49
$3100F_2$	8241.06 [23]	0.31	1.63		0.60
$2200A_1$		8309.66	8308.22		8308.88
$2200F_2$	8310.30 [29]	0.21	2.07		0.98
$2110F_2$	8378.60 [29]	0.27	1.89		-0.33
$2110A_1$	8380.10 [23]	0.44	3.27		3.08
$5000A_1$	9875.78[29]	3.71	4.81		0.92
$5000F_2$	9875.78[29]	3.71	4.81		0.92
$4100A_1$	10148.10 [25]	0.26	2.55		-0.71
$4100F_2$	10148.10 [25]	0.24	2.55		-0.73
$6000A_1$	11647.23 [25]	5.53	7.19	-0.02	0.66
$6000F_2$	11647.23 [25]	5.53	7.19	-0.02	0.66
$7000A_1$	13352.66 [25]	9.57	11.91	0.82	2.10
$7000F_2$	13352.66 [25]	9.57	11.91	0.82	2.10
$8000A_1$		14976.84	14973.69		14987.35
$8000F_2$		14976.84	14973.69		14987.35
$^{74}\mathrm{GeD}_4$					
$1000A_1$	1509.40[29]	2.30	2.11		2.68
$1000F_2$	1522.70[29]	2.30	2.10		2.68
$2000F_2$	3003.52[29]	5.41	5.31		5.71

4 Conclusions

We have developed a general variational method for treating the stretch-only vibrational motions of XY_4 systems. Particularly 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. 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 five dimensional bend-only problem, is discussed in the following paper [9].

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