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Variational Calculations of Rotational−Vibrational Energies of CH_4 and Isotopomers Using an Adjusted ab Initio Potential

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We report variational calculations of vibrational energies of CH_4, CH_3D, CH_2D_2, CHD_3, and CD_4 using the code "Multimode" and the ab initio force field of Lee and co-workers [Lee, T. J.; Martin, J. M. L.; Taylor, P. R. *J. Chem. Phys*. **1995**, *102*, 254], re-expressed using Morse variables in the stretch displacements. Comparisons are made with experimental energies for CH_4 with this potential, and then small adjustments are made to the potential to improve agreement with experiment for CH_4. Calculations for the isotopomers are done using the adjusted potential and compared with experiment. Additional vibrational energies and assignments not reported experimentally are also given for CH_4 and the isotopomers. Exact rotational−vibrational energies of CH_4 are also reported for $J = 1$.

1. Introduction

The spectroscopy of methane, CH_4, and isotopomers, CD_4, CH_3D, CD_3H, and C_2D_2 has been extensively studied for over 30 years.[1] Theoretical work has included a number of ab initio force fields,[2] culminating in the most accurate one by Lee, Martin, and Taylor (LMT).[3] The first calculations of the vibrational energies in nine degrees of freedom were done by Leforestier and Iung for CD_3H, who focused on the CH-stretch overtones.[4] They used an approximate, normal coordinate Hamiltonian and a force field in which the interaction terms were limited to two-mode coupling, and the order of coupling was limited to 4 or less. Eigenvalues were determined by the Lanczos method. More recently, Wyatt and Iung[5] used the potential of Leforestier and Iung in a study of the time dependence of high CH-stretch overtones in CD_3H. Halonen[6] has recently reported an extensive treatment of CH_4 vibrations using second-order perturbation theory. More recently Halonen and co-workers[7] have made modification to the LMT potential, using second-order Van Vleck perturbation theory, to bring theory into agreement with experiment for the vibrational energies of CH_4. A similar study, however, using fourth-order Van Vleck perturbation theory has also been done very recently by Wang and Sibert,[8] and applied to CH_4 and eight isotopomers. All of these calculations were done for zero total angular momentum.

We recently reported variational calculations of the fundamentals, and low-lying combination and overtone states of CH_4 and isotopomers CD_4, CH_3D, CD_3H, and C_2D_2 using the LMT potential. Exact calculations for $J = 1$ were also reported for CH_4. These calculations were done using the code "Multimode"[10] which obtains rotational−vibrational (rovibrational) energies and wave functions using vibrational self-consistent field and variational methods. The comparisons with experiment for the vibrational energies showed very good agreement, with the exception of calculated CH-stretch fundamentals, which exceeded the experimental ones by approximately 30 cm^{-1}. This failing was traced to the representation of the potential in (symmetry) bond displacement coordinates. Results for the fundamentals of CH_4, using Morse variables for the stretches, showed expected improved agreement with experiment for the stretches. The rovibrational calculations of the fundamentals of CH_4 for $J = 1$ produced rotation and Coriolois coupling constants in very good agreement with experiment. The expected large Coriolis interaction for $\nu_4(F_2)$ was nicely reproduced by the calculations.

In this paper we present additional comparisons between theory and experiment for CH_4 using the Morse version of the LMT potential. Modifications of this potential are made to improve agreement with experiment, and the adjusted potential is applied to CH_4 up to the second CH-stretch overtone, and to the isotopomers CD_4, CH_3D, CD_3H, and C_2D_2. Many unmeasured excitaition energies are also reported using the modified potential. An exact $J = 1$ calculation is also reported using the new potential for the fundamentals of CH_4.

In the next section the methods used in "Multimode" are briefly reviewed and the bases used in the vibrational calculations are described. The potential is described in section 3 and results and discussion of calculations using the Morse and adjusted Morse versions of the LMT potential are given in section 4. We summarize and make concluding remarks in section 5.

2. Details of the Calculations

The full Watson Hamiltonian in N mass-scaled normal modes Q_i is used in "Multimode", and the potential is represented by the following hierarchical representation:

$$V(Q_1,Q_2,...,Q_N) = \sum_i V_i^{(1)}(Q_i) + \sum_{ij} V_{ij}^{(2)}(Q_i,Q_j) + \sum_{ijk} V_{ijk}^{(3)}(Q_i,Q_j,Q_k) + \sum_{ijkl} V_{ijkl}^{(4)}(Q_i,Q_j,Q_k,Q_l) \quad (1)$$

In the one-mode terms $V_i^{(1)}(Q_i)$, only one coordinate varies, in the two-mode terms $V_{ij}^{(2)}(Q_i,Q_j)$, two coordinates vary, etc.

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Matrix elements of the potential are performed using numerical quadratures at optimized quadrature points (determined by the one mode terms), and at most four-dimensional quadrature is required. All of the vibrational calculations begin with a vibrational self-consistent field (VSCF) approach,[11,12] and there are two options to do "CI" calculations. One CI is based on mixing a group of VSCF states. The second CI method, denoted VCI, uses the orthonormal basis of eigenfunctions of a single VSCF Hamiltonian, usually the one for the ground state. More details of the methods can be found in ref 9.

As shown previously[9] the calculations using the four-mode representation of the potential appear to be well converged, i.e, to within a wavenumber of less, at least for the low-lying energies considered. (The two-mode representation of the potential for CH_4 was adequate for most modes; however, it produced errors as large as 80 cm^{-1} for the CH-stretch fundamentals.) Thus, only four-mode calculations are reported here.

The details of the VCI calculation are exactly as described in detail previously,[9] so we omit giving them here. Presently, "Multimode" can exploit symmetry for the C_{2v} and D_{2h} point groups. For CH_4 and all the isotopomers C_{2v} symmetry was used. Three basis sizes were used for the CH_4 calculations: 5868, 6652, and 9316 for A states; 5346, 5836, and 8416 for B_1 and B_2 states; and 4831, 5167, and 7423 for A_2 states. For the isotopomers the smallest of the three bases was used.

3. Results and Discussion

The Potential. The results given previously by us for CH_4 and its isotopomers were obtained using the original potential of Lee, Martin, and Taylor,[3] which is given as a fourth-order Taylor series expansion in the symmetry displacement coordinates of Gray and Robiette.[13] The accuracy of the results for the fundamentals is excellent, with the exception of the C−H fundamentals, ν_1 and ν_3, which are high by 31 and 33 cm^{-1}, respectively. It is well-known that X−H stretching vibrations, evaluated variationally using numerical quadrature to integrate Taylor expansion potentials, are overestimated,[14] sometimes by as much as 60 cm^{-1}. The reason for this is the H-atom moves to relatively large displacements on the quadrature grid and well beyond the range described by the anharmonic boundary of the truncated (usually at quartic) potential.

To overcome this deficiency, either a Taylor expansion to sextic (say), or a potential which extrapolates more accurately to large bond distances should be used in the X−H stretch coordinate. The latter approach is usually preferred, implemented by adopting either a Simons−Parr−Finlan[15] coordinate, $(R - R_e)/R$, or a Morse[16] coordinate, $1 - \exp[\alpha(R - R_e)]$, to replace the displacement coordinate $R - R_e$ for the stretching modes in the Taylor expansion. Either replacement results in an expansion that is of infinite order in the stretch coordinate $R - R_e$.

We have converted the LMT potential to Morse form in the stretching modes. To do this, we have left the symmetry coordinates for the bending vibrations intact, but we have expanded the symmetry coordinates for the stretching vibrations to pure bond displacements $(R - R_e)$ using the expressions given by Raynes et al.[2] Our coordinates are thus R_1, R_2, R_3, R_4 for the stretches and S_{2a}, S_{2b}, S_{4x}, S_{4y}, S_{4z} for the bends, and we have converted the stretch part to Morse form using the parameter $\alpha = 1$/bohr.

The vibrational energies for the parent molecule CH_4 using this potential are given in Table 1 and compared with a selection of experimental results. The variational results used a four-mode representation of the potential and Coriolis terms and the smallest of the three bases described above. On the basis of our previous calculations where a comparison of two-, three-, and four-mode representations were done, we are confident that the present results are converged to better than 1 cm^{-1}. There are two main observations. First, there is an overcompensation of 3.2 cm^{-1} in ν_1 and an overcompensation of 7.5 cm^{-1} in ν_3 on converting to Morse in the C−H stretch coordinate; the fundamentals ν_2 and ν_4, however, remain almost exact. Second, for the overtone $2\nu_3$, there is a systematic underestimation of experimental results by 5−9 cm^{-1} for the E and A_1 components. For the overtone $2\nu_4$, theory is low by 4.7 and 2.5 cm^{-1} for the A_1 and F_2 states, respectively, but high by 4 cm^{-1} for the E states. The error in $2\nu_1$ is approximately twice that in ν_1, and the spread between the E and A_1 components for $2\nu_2$ is about right, but the midpoint energy is low by about 3 cm^{-1}. There is also one large error of 14 cm^{-1} in the combination band $\nu_1 + \nu_2$. These errors are magnified for higher overtones and combinations in other regions of the spectrum. In general though the agreement between theory and experiment is quite good, which is due to the high quality of the LMT potential.

TABLE 1: Comparison of Calculated and Experimental Energies (cm^{-1}) for Nonrotating CH_4[a]

symmetry	state	exptl	theory
F_2	0001	1310.8	1310.9
E	0100	1533.3	1532.3
A_1	0002	2587.0	2582.3
F_2	0002	2614.3	2611.8
E	0002	2624.6	2628.8
F_2	0101	2830.3	2830.5
F_1	0101	2846.1	2845.3
A_1	1000	2916.5	2913.2
F_2	0010	3019.5	3011.3
A_1	0200	3063.6	3060.4
E	0200	3065.1	3062.4
F_2	1001	4223.5	4222.9
F_2	0011	4319.2	4311.0
E	0011	4322.15	4315.2
F_1	0011	4322.6	4318.0
A_1	0011	4322.7	4320.7
E	1100	4446.4	4432.6
F_1	0110	4537.6	4530.8
F_2	0110	4543.8	4537.8
A_1	2000	5790.0	5785.0
A_1	0020	5968.1	5962.3
F_2	0020	6004.6	5999.4
E	0020	6043.8	6034.5

[a] The calculations were performed with the unadjusted Morse representation of the LMT potential.

We have carried out a manual adjustment of the force field in a systematic way. At all times, we adjusted the most recent potential in symmetrized displacement coordinates and then followed this by a subsequent conversion to Morse coordinates for the stretches. We first adjusted only the harmonic force constants by an amount $(\nu(\mathrm{exptl})/\nu(\mathrm{calcd}))^2$ and recalculated the CH_4 spectrum. We looked, in particular, at the changes in the errors of the two-quanta levels given above. We then tackled these errors one at a time, by varying the relevant quartic force constants; F_{1111} is responsible for $2\nu_1$, $F_{2a2a2a2a}$ is responsible for the mean of $2\nu_2$, while $F_{2a2a2b2b}$ modifies the spread. Similarly, for $2\nu_3$ and $2\nu_4$, the relevant force constants are $F_{3x3x3x3x}$, $F_{3x3x3y3y}$ and $F_{4x4x4x4x}$, $F_{4x4x4y4y}$, respectively. Finally, for $\nu_1 + \nu_2$, F_{112a2a} must be adjusted. After adjusting the quartic force constants responsible for a particular two-quantum state, we reevaluated the harmonic force constants. This process was repeated twice for the complete set of levels above. The final

TABLE 2: Comparison of the Force Constants for the Symmetrized Internal Coordinates Derived by Lee, Martin, and Taylor (LMT) [ref 2] with Those Adjusted in This Work[a]

force constant	LMT	this work
F_{11}	5.468 649 239 1	5.473 573 5
$F_{2a2a} = F_{2b2b}$	0.579 185 267 6	0.579 404 7
$F_{3x3x} = F_{3y3y} = F_{3z3z}$	5.366 023 687 5	5.387 574 3
$F_{4x4x} = F_{4y4y} = F_{4z4z}$	0.532 266 747 4	0.529 499 4
F_{1111}	37.417 102 951 7	37.0
$F_{112a2a} = F_{112b2b}$	−0.012 643 269 8	+0.192 6
$F_{3x3x3x3x} = F_{3y3y3y3y} = F_{3z3z3z3z}$	41.047 029 303 0	40.047
$F_{3x3x3y3y} = F_{3x3x3z3z} = F_{3y3y3z3z}$	41.140 327 914 5	40.14
$F_{4x4x4x4x} = F_{4y4y4y4y} = F_{4z4z4z4z}$	0.498 755 194 1	0.398 755
$F_{4x4x4y4y} = F_{4x4x4z4z} = F_{4y4y4z4z}$	0.709 767 007 0	0.959 767

[a] Units are aJ/A**n.

symmetrized force constants that differ from the original ones of Lee, Martin, and Taylor are given in Table 2, and the results for CH_4 are discussed below.

CH_4. The CH_4 energy levels using the adjusted force field in Table 2 are given in Table 3, and we also present predictions using this force field in Table 4. Note first that the calculated energies appear to be well converged even for the smallest basis. The agreement between theory and all available experimental data is overall quite good with one exception indicated. The average error, excluding the 0102(A_2) state, is 2.2 cm^{-1}. For that state an examination of the eigenvector indicates that basis functions that differ in excitation of five modes contribute significantly to the eigenvector, and so the present four-mode representation of the potential is not adequate for this state. Also, there are fairly large differences between theory and experiment for the 0111 states.

The predictions in Table 4 are compared with previous predictions based on a spectroscopic Hamiltonian of Georges et al.[1] and several predictions based on very recent perturbation theory calculations.[7,8] In general there is much less agreement between the present calculations and those based on the experimental spectroscopic Hamiltonian than between the present calculations and experiment. The agreement with the predictions of perturbation theory are good.

To understand the possible source of disagreement with the predictions of the spectroscopic Hamiltonian it is useful to return to the comparisons with experiment in Table 3. Apart from the large error of 30 cm^{-1} for 0102(A_2) in Table 3, resulting from the large contributions of second-order five-mode coupling terms in the potential, there are only three levels with an error greater than 15 cm^{-1}. These are 1010(F_2) (18 cm^{-1}), 0111(F_2) (21 cm^{-1}), and 0030(F_1) (18 cm^{-1}). These are due to residual force field errors; we found that there were very subtle dependencies of force constants on 1010 and 0111, and could not refine these confidently by hand. A least-squares algorithm is really required for these fine adjustments to the cross-terms in the potential. We did not include 0030 in our refinement as it required such a large basis for convergence. The remaining comparisons suggest that the force field has otherwise been successfully refined.

TABLE 3: Theoretical and Experimental Vibrational Energies (cm^{-1}) for CH_4 Using the Adjusted Morse Potential. Theoretical Results for Three Different Bases Are Given

symmetry	state	exptl[a]	I[b]	II[c]	III[d]
F_2	0001	1310.76	1310.6	1310.6	1310.6
E	0100	1533.33	1533.7	1533.7	1533.7
A_1	0002	2587.04	2584.0	2584.0	2584.0
F_2	0002	2614.26	2615.4	2615.4	2615.4
E	0002	2624.62	2624.1	2624.1	2624.1
F_2	0101	2830.32	2831.8	2831.8	2831.8
F_1	0101	2846.08	2846.5	2846.5	2846.5
A_1	1000	2916.48	2916.1	2916.1	2916.1
F_2	0010	3019.49	3018.0	3018.0	3018.0
A_1	0200	3063.65	3063.8	3063.8	3063.8
E	0200	3065.14	3065.5	3065.5	3065.5
F_2	0003	3870.49	3865.7	3865.5	3865.4
A_1	0003	3909.18	3914.9	3914.7	3914.6
F_1	0003	3920.50	3925.9	3925.9	3925.8
F_2	0003	3930.92	3933.3	3933.2	3933.2
E	0102	4105.15	4102.0	4101.4	4101.3
F_1	0102	4128.57	4131.6	4131.5	4131.5
A_1	0102	4132.99	4141.6	4141.6	4141.5
F_2	0102	4142.86	4145.3	4145.3	4145.3
E	0102	4151.22	4155.6	4155.6	4155.6
A_2	0102	4161.87	4190.7[e]	4190.8[e]	4190.8[e]
F_2	1001	4223.46	4225.4	4225.4	4225.4
F_2	0011	4319.21	4317.5	4317.5	4317.4
E	0011	4322.15	4322.9	4321.6	4321.6
F_1	0011	4322.58	4324.4	4322.9	4321.4
A_1	0011	4322.72	4326.3	4326.3	4326.2
F_2	0201	4348.77	4351.0	4351.0	4351.0
F_1	0201	4363.31	4369.3	4369.3	4369.3
F_2	0201	4379.10	4378.9	4378.9	4378.9
E	1100	4446.41	4438.4	4438.4	4438.4
F_1	0110	4537.57	4539.0	4539.0	4538.9
F_2	0110	4543.76	4545.0	4545.0	4544.9
E	0300	4592.03	4592.5	4592.5	4592.5
A_2	0300	4595.32	4598.1	4598.1	4598.1
A_1	0300	4595.56	4598.6	4598.6	4598.6
F_2	0012	5587.98	5588.2	5587.8	5588.1
F_2	0012	5623.00	5619.8	5619.4	5619.7
F_2	0012	5628.39	5628.2	5627.9	5628.1
A_1	2000	5790.00	5790.3	5789.9	5789.8
F_2	1010	5819.72	5839.3	5838.9	5838.4
F_2	0111	5826.65	5847.4	5847.4	5847.3
A_1	0020	5968.10	5971.2	5970.9	5970.9
F_2	0020	6004.60	6008.7	6008.6	6008.6
E	0020	6043.80	6042.9	6042.8	6042.8
F_2	0210	6054.64	6060.5	6061.1	6060.0
F_2	0210	6065.32	6065.1	6065.0	6064.6
F_2	0030	8906.78	8918.5	8617.0	8915.5
F_1	0030	8947.95	8967.8	8967.3	8965.8
A_1	1400	8975.34	8976.2	8973.8	8972.5
F_2	0030	9045.92	9046.8	9045.5	9044.5

[a] Taken from refs 6−8. [b] Basis size = 5868 (A_1), 5346 (B_1 and B_2), 4831 (A_2). [c] Basis size = 6652 (A_1), 5836 (B_1 and B_2), 5167 (A_2).[d] Basis size = 9316 (A_1), 8416 (B_1 and B_2), 7423 (A_2). [e] Significant five-mode coupling, energy probably not converged.

Turning now to Table 4, we see that the remaining levels in the 0111 manifold are also in error with the predictions of ref 1, although the two PT predictions suggest that the highest F_2 level is quite accurate. These levels are the eigenfunctions of a complicated 8 × 8 matrix (in the absence of second-order mixing with other states), and we obviously have not reproduced the lower levels accurately. However, it should be emphasized that even the F_2 level of ref 1 is 13 cm^{-1} lower than the F_2 levels obtained from the PT predictions. For the remaining two PT predictions for the two F_2 components of 0301, our results are slightly closer than those of ref 1. Hence, all three of our levels are very close to those of the PT predictions. For the remaining levels in Table 4, the comparisons are in general, rather erratic, and this may be partly due to the difficulty we have with degenerate levels. We have already said that the presence of second-order, five-mode terms makes it difficult to accurately assign such levels, and this situation will become worse as we progress up the spectrum. On the other hand, we are confident that the levels within each manifold are correct. It should also be pointed out that, as the number of F and E level excitations increases, the larger will become the matrix to be diagonalized, and the 1:1 relationship between force

TABLE 4: Predicted Vibrational Energies for CH_4 (cm^{-1}) Using the Adjusted Morse Force Field and Comparisons with Predictions Based on a Spectroscopic Hamiltonian (SH) and Perturbation Theory

symmetry	normal	SH[a]	present	PT[b]	PT[c]
A_1	0004	5121.3	5109.5		
F_2	0004	5143.2	5136.6		
E	0004	5167.2	5163.8		
F_2	0004	5211.3	5222.9		
E	0004	5228.9	5240.2		
F_1	0004	5230.8	5260.1		
A_1	0004	5240.0	5248.2		
F_2	0103	5377.0	5376.2		
F_1	0103	5393.7	5405.8		
E	0103	5424.7	5459.5		
F_2	0103	5429.6	5455.2		
F_1	0103	5436.8	5467.0		
F_2	0103	5445.1	5477.8[d]		
F_1	0103	5462.9	5511.4		
A_1	1002	5486.4	5494.2		
F_2	1002	5517.2	5542.6		
E	1002	5532.2	5536.9		
A_1	0012	5606.3	5636.2		
F_1	0012	5617.9	5638.5		
E	0012	5625.2	5641.0		
F_1	0012	5632.0	5653.4		
A_1	0202	5616.4	5614.4		
E	0202	5618.2	5621.6		
F_2	0202	5640.6	5649.6		
E	0202	5653.6	5664.6		
F_1	0202	5655.3	5693.2		
A_2	0202	5662.3	5697.6[d]		
F_2	0202	5668.9	5670.2[d]		
A_1	0202	5682.4	5686.7		
E	0202	5691.4	5726.0		
F_2	1101	5729.7	5743.5		
F_1	1101	5756.0	5766.0		
F_1	0111	5827.2	5849.4		
A_1	0111	5831.3	5857.6		
A_2	0111	5831.8	5853.8		
E	0111	5837.0	5858.3[d]		
E	0111	5841.0	5866.0		
F_1	0111	5845.8	5874.1		
F_2	0111	5849.2	5867.6	5862.7	5862.4
F_2	0301	5867.6	5871.1	5871.2	5868.7
F_1	0301	5879.0	5917.9		
F_2	0301	5894.1	5893.0	5893.2	5892.1
F_1	0301	5909.7	5914.9		
A_1	1200	5971.5	5941.7		
E	1200	5974.5	5957.9		
F_1	0210	6059.3	6064.5		
A_1	0400	6116.7	6118.4		
E	0400	6118.6	6119.8		
E	0400	6124.1	6127.8		

[a] Reference 1. [b] Reference 7. [c] Reference 8. [d] Significant five-mode coupling, energy probably not converged.

constant and vibrational level will almost completely disappear. A combination of the above two effects can best be seen in the comparisons for 0004 and 0400. These represent our "cleanest" levels and are the least affected by five-mode couplings. However, there are seven levels for 0004 since this involves four quanta of an F state, but there are only three levels for 0400 as this involves four quanta of an E state. The latter are clearly more consistent with the predictions of ref 1 than those of the former.

It is clear that a more complete refinement of the CH_4 force field is required, preferably using a least squares module, and with the inclusion of at least five-mode coupling. This will be attempted in due course.

CD_4. Vibrational energies of CD_4 and other isotopomers were done with the potential adjusted to give improved agreement with experiment for CH_4. The variational calculations for CD_4 were done with a relatively small basis of order 5868 for A_1 states, 5346 for B_1 and B_2 states, and 4831 for A_2 states.

TABLE 5: Theoretical and Experimental Vibrational Energies (cm^{-1}) for CD_4 Using the Adjusted Morse Representation of the LMT Potential

symmetry	state	exptl[a]	theory
F_2	0001	997.8	997.0
E	0100	1091.7	1091.7
A_1	0002	1965.5	1963.3
F_2	0002	1990.5	1990.1
E	0002	1996.8	1994.6
F_2	0101	2083.4	2083.7
F_1	0101	2090.9	2090.6
A_1	1000	2101.4	2100.9
A_1	0200	2182.2	2182.1
E	0200	2182.6	2182.6
F_2	0010	2260.1	2258.5
F_2	0020	4493.7	4493.2

[a] Gray, D. L.; Robiette, A. G. *Mol. Phys.* **1979**, *37*, 1901.

TABLE 6: Theoretical Vibrational Energies (cm^{-1}) for CD_4 Using the Adjusted Morse Representation of the LMT Potential

symmetry	state	theory	symmetry	state	theory
F_2	0003	2940.3	A_1	0202	4133.5
A_1	0003	2979.0	E	0202	4152.7
F_1	0003	2984.9	F_2	0202	4166.2
F_2	0003	2988.6	E	0202	4168.9
E	0102	3048.9	F_2	0202	4176.4
F_1	0102	3075.0	A_2	0202	4184.3
A_1	0102	3079.8	F_1	0202	4186.9
F_2	0102	3080.7	E	0202	4198.7
E	0102	3085.7	A_1	2000	4190.8
A_2	0102	3105.7	F_2	1101	4190.9
F_2	1001	3103.9	F_1	1101	4200.8
F_2	0201	3169.1	F_2	0012	4212.2
F_2	0201	3177.9	F_2	0012	4240.2
F_1	0201	3194.1	F_2	0012	4243.6
E	1100	3248.9	A_1	0012	4251.8
E	0011	3250.3	E	0012	4252.0
F_1	0011	3252.6	F_1	0012	4249.1
A_1	0011	3254.2	F_1	0012	4249.1
E	0300	3271.8	F_2	0301	4254.2
A_2	0300	3273.9	F_1	0301	4266.2
A_1	0300	3274.2	F_1	0301	4279.1
F_1	0110	3343.2	F_2	0301	4286.3
F_2	0110	3346.1	A_1	1200	4271.7
A_1	0004	3891.1	E	1200	4272.3
F_2	0004	3912.3	F_2	1010	4330.2
E	0004	3924.9	E	0111	4338.3
F_2	0004	3971.3	F_2	0111	4340.1
E	0004	3979.9	E	0111	4342.8
A_1	0004	3984.3	F_1	0111	4343.1
F_1	0004	3991.9	F_2	0111	4349.3
F_2	0103	4025.0	A_1	0111	4350.6
F_1	0103	4035.0	F_1	0111	4349.8
E	0103	4078.7	A_2	0111	4353.4
F_2	0103	4079.7	A_1	0400	4360.7
F_1	0103	4083.8	E	0400	4361.3
F_1	0103	4089.5	E	0400	4363.9
F_2	0103	4099.0	F_2	0210	4425.6
A_1	1002	4065.8	F_2	0210	4429.8
F_2	1002	4098.0	F_1	0210	4439.9
E	1002	4106.9	A_1	0020	4458.5
A_1	0202	4132.2	E	0020	4521.5

Table 5 contains a comparison of theory and experiment for CD_4 vibrational energies. As seen the agreement with experiment is excellent. The average error in the calculated energies is less than 1 cm^{-1}. An extensive set of all the calculated energies and assignments is given in Table 6 up to just over 4500 cm^{-1}.

TABLE 7: Theoretical and Experimental Vibrational Energies (cm^{-1}) for CD_2H_2 Using the Adjusted Morse Representation of the LMT Potential

state	exptl[a]	theory
000 100 000	1033.1	1033.1
000 000 100	1091.2	1090.2
000 000 001	1236.3	1236.1
000 010 000	1331.4	1331.6
001 000 000	1435.1	1434.8
000 200 000	2054.2	2053.7
000 100 100	2124.7	2126.6
000 000 200	2145.7	2143.2
010 000 000	2203.2	2202.8
000 000 010	2234.7	2234.4
000 100 001	2286.0	2287.7
000 000 101	2330.7	2329.5
000 000 002	2458.8	2459.4
001 100 000	2469.2	2470.4
001 000 100	2510.2	2515.8
000 010 001	2560.6	2561.5
000 020 000	2658.3	2658.4
001 000 001	2671.7	2671.8
002 000 000	2855.7	2854.7
100 000 000	2975.5	2974.0
000 001 000	3012.3	3010.0
001 001 000	4425.6	4424.5
000 002 000	5999.1	5996.8

[a] Gray, D. L.; Robiette, A. G. *Mol. Phys.* **1979**, *37*, 1901.

CD_2H_2. The vibrational calculations were done with same bases used for CD_4. The comparison between theory and experiment for CD_2H_2 is given in Table 7 for energies up to nearly 6000 cm^{-1}. As seen the agreement with experiment is very good. The average error in the calculations is less than 2 cm^{-1}. A list of all the calculated energies up to nearly 5000 cm^{-1} is given in Table 8.

CH_3D and CHD_3. The bases for vibrational calculations for these molecules was 5352 and 4573 for A_1 and B_2 states, respectively. These molecules are of C_{3v} symmetry and the reduction to C_{2v} leads to states of A_1 and A_2 symmetry only.

The comparison with experiment for CH_3D is given in Table 9, where excellent agreement is seen. Calculated energies and assignments not included in Table 9 up to 4817.9 cm^{-1} are given in Table 10. Comparison with experiment for CHD_3 is shown in Table 11, where, again, very good agreement is seen. Additional calculations and assignments for CHD_3 are given in Table 12.

All of the calculations for all the isotopomers included eigenvectors. These are very useful in determining the extent of mixing among zero-order states and they are available upon request.

CH_4 $J = 1$. Rovibrational calculations of the fundamentals of CH_4 were performed using the adjusted Morse force field for $J = 1$. The methods employed in these calculations have been described previously.[9,10d] Calculations are first done for the diagonal blocks, labeled by the usual K_a quantum number, and these these blocks are coupled together by the usual nondiagonal terms in the Watson Hamiltonian, e.g., Coriolis coupling. Exact calculations for $J > 0$ are very computer intensive and so smaller bases, of the order of 1000 for each symmetry block, were used with the four-mode representation of the potential and moment of inertia. The results are given in Table 13, along with available experimental data. We have chosen to give the absolute energies rather than energy differences relative to the $J = 0$ energies in order to make a rigorous comparison with experiment.

TABLE 8: Theoretical Vibrational Energies (cm^{-1}) for CD_2H_2 Using the Adjusted Morse Representation of the LMT Potential

state	theory	state	theory	state	theory
000 110 000	2366.3	001 010 001	4016.9	010 000 002	4610.0
000 010 100	2422.7	000 101 000	4043.4	001 100 200	4623.5
001 010 000	2766.8	100 000 100	4056.3	001 000 300	4630.4
000 300 000	3066.1	000 400 000	4071.4	000 100 102	4642.9
000 200 100	3142.7	000 001 100	4090.0	010 010 100	4643.5
010 100 000	3184.7	002 000 001	4092.2	000 210 001	4658.4
000 000 300	3207.2	001 020 000	4093.8	000 000 012	4659.4
000 100 200	3237.0	000 300 100	4156.5	011 100 000	4668.2
000 100 010	3245.1	002 010 000	4187.1	000 010 110	4671.1
010 000 100	3307.2	010 000 200	4196.3	000 000 202	4680.2
000 200 001	3316.6	100 000 001	4203.9	001 100 010	4694.3
000 000 110	3327.7	000 001 001	4235.8	000 220 000	4714.8
010 000 001	3381.6	010 200 000	4242.8	010 010 001	4720.1
000 210 000	3386.9	000 200 010	4246.7	011 000 100	4731.4
000 100 101	3398.1	000 100 300	4261.1	000 100 003	4748.5
000 000 201	3441.1	003 000 000	4262.8	000 110 101	4753.0
000 000 011	3450.8	000 200 200	4263.8	001 000 110	4762.2
010 010 000	3474.4	100 010 000	4298.5	001 200 001	4771.7
000 110 100	3482.9	020 000 000	4316.2	000 010 011	4784.0
001 200 000	3484.9	000 011 000	4330.1	000 010 201	4786.4
000 100 002	3526.4	000 300 001	4334.6	000 000 103	4788.0
000 010 200	3532.1	010 100 100	4348.5	010 020 000	4800.4
000 000 102	3557.8	010 000 010	4350.4	000 120 100	4814.0
000 010 010	3561.8	000 100 110	4353.2	001 000 201	4823.7
001 000 200	3567.5	000 310 000	4402.7	001 210 000	4837.6
001 100 100	3573.3	101 000 000	4402.9	000 110 002	4846.3
000 110 001	3626.0	000 000 400	4413.3	000 020 200	4856.6
011 000 000	3628.8	000 200 101	4421.2	001 100 101	4868.0
010 000 010	3669.4	000 000 210	4422.1	011 000 001	4875.7
000 010 101	3676.3	010 100 001	4442.7	000 020 010	4880.8
000 000 003	3683.9	000 200 002	4444.1	000 000 004	4885.5
000 120 000	3694.2	000 000 301	4463.0	002 200 000	4900.4
001 100 001	3737.6	000 000 020	4487.2	001 000 011	4913.4
000 020 100	3750.5	000 210 100	4495.8	001 010 200	4915.7
000 010 002	3761.2	001 300 000	4501.5	001 110 100	4926.0
001 000 101	3791.0	000 100 201	4505.4	000 120 001	4951.6
001 110 000	3822.5	010 110 000	4531.6	001 010 001	4968.9
001 010 100	3858.1	000 010 300	4551.7	000 010 003	4969.9
000 210 000	3881.5	010 000 101	4554.8	002 000 200	4976.3
000 020 001	3888.5	000 000 111	4562.7	002 100 100	4979.5
001 000 002	3902.2	000 100 011	4570.5	001 100 002	4979.6
002 000 100	3927.1	001 200 100	4573.9		
000 030 000	3981.0	000 110 010	4588.4		
100 100 000	4006.4	000 110 200	4589.8		

TABLE 9: Calculated and Experimental Vibrational Energies (in cm^{-1}) of CH_3D

symmetry	state	exptl[a]	theory
E	000 001	1161.1	1160.6
A_1	001 000	1306.8	1306.9
E	000 010	1472.0	1472.0
A_1	010 000	2200.0	2198.9
A_1	000 002	2316.3	2315.9
E	000 002	2323.3	2323.1
E	001 001	2467.0	2467.8
A_1	002 000	2597.7	2597.9
E	000 011	2623.4	2624.9
A_1	000 011	2633.2	2634.1
A_2	000 011	2634.8	2634.8
E	001 010	2776.3	2777.5
A	000 020	2910.1	2909.3
E	000 020	2940.1	2939.9
A_1	100 000	2969.5	2968.9
E	000 100	3016.7	3014.2

[a] Nikitin, A.; Champion, J. P.; Tyuterev, Vl. G.; Brown, L. R. *J. Mol. Spectrosc.* **1997**, *184*, 120.

As expected the diagonal energies show spherical top behavior, i.e., there is a 3-fold degeneracy in the rovibrational energies. These rovibrational energies are in good agreement with exact, coupled ones, for the $J = 1$ zero point energy and the $\nu_1(A_1)$ and $\nu_2(E)$ fundamentals. However, for the two F_2

TABLE 10: Calculated Vibrational Energies (in cm^{-1}) of CH_3D

symmetry	state	theory	symmetry	state	theory
			E	000 101	4170.4
E	010 001	3342.7	A_2	000 101	4177.3
A_1	000 003	3472.0	A_1	001 020	4217.4
A_2	000 003	3472.4	E	001 020	4243.3
E	000 003	3489.8	A_1	101 000	4273.0
A_1	011 000	3501.2	E	001 100	4314.1
A_1	001 002	3621.3	A_1	020 000	4342.0
E	001 002	3629.7	E	100 010	4358.5
E	010 010	3670.0	A_2	000 030	4405.1
E	002 001	3760.0	A_1	000 030	4406.6
E	000 012	3781.6	E	000 030	4441.1
E	000 012	3784.7	E	000 110	4470.8
A_2	000 012	3814.7	A_2	000 110	4475.3
A_1	000 012	3815.3	A_1	000 110	4486.3
A_1	003 000	3873.0	A_1	010 002	4476.2
E	001 011	3949.3	E	010 002	4488.8
A_2	001 011	3959.1	A_1	000 004	4624.2
A_1	001 011	3959.7	A_1	000 004	4632.5
E	000 021	4059.6	A_2	000 004	4639.1
A_1	000 021	4089.6	E	000 004	4660.8
A_2	000 021	4091.0	E	011 001	4664.4
E	000 021	4117.5	E	001 003	4782.5
E	002 010	4069.8	A_1	012 000	4787.2
E	100 001	4124.0	A_2	001 003	4816.6
A_1	000 101	4162.5	A_1	001 003	4817.9

TABLE 11: Calculated and Experimental Vibrational Energies (in cm^{-1}) of CHD_3

symmetry	state	exptl	theory
A_1	001 000	1004.5[a]	1003.5
E	000 001	1035.9[a]	1035.5
E	000 010	1292.5[a]	1292.2
A_1	002 000	1991.1[a]	1989.5
E	001 001	2041.4	2041.1
E	000 002	2067.6	2066.3
A_1	010 000	2142.6[a]	2142.0
E	000 100	2250.9[a]	2248.9
E	001 010	2301.2	2300.7
A_1	000 020	2564.6[a]	2564.6
E	000 020	2586.1[a]	2585.8
A_1	100 000	2992.2[a]	2991.3
E	001 001	4262.1[b]	4262.1
A_1	010 020	4697.1[b]	4703.9
A_1	110 000	5134.9[b]	5137.9

[a] Gray, D. L.; Robiette, A. G. *Mol. Phys.* **1979**, *37*, 1901. [b] Lewerenz, M.; Quack, M. *J. Chem. Phys.* **1988**, *88*, 5408.

TABLE 12: Calculated Vibrational Energies (in cm^{-1}) of CHD_3

symmetry	state	theory	symmetry	state	theory
A_1	000 002	2058.9	A_2	000 012	3351.9
A_1	000 011	2325.6	E	000 012	3359.1
A_2	000 011	2328.7	E	000 012	3372.1
E	000 011	2329.2	E	010 010	3432.0
A_1	003 000	2963.8	A_1	000 110	3523.1
E	002 001	3023.0	E	000 110	3533.0
A_1	001 002	3071.4	A_2	000 110	3549.0
E	001 002	3073.2	A_1	001 020	3579.1
E	000 003	3081.8	E	001 020	3595.5
A_1	000 003	3092.8	A_2	000 021	3599.9
A_2	000 003	3093.3	A_1	000 021	3602.8
A_1	011 000	3155.2	E	000 021	3621.7
E	010 001	3178.9	E	000 021	3636.2
E	001 100	3239.1	E	000 030	3840.3
E	000 101	3277.3	A_2	000 030	3882.0
A_2	000 101	3280.6	A_1	000 030	3882.8
A_1	000 101	3286.9	A_1	004 000	3929.2
E	001 010	3293.2	A_1	101 000	3986.6
A_1	001 011	3346.4	E	003 001	4000.6
E	001 011	3348.9	E	100 001	4028.0
A_2	001 011	3349.9	A_1	002 002	4045.0
A_1	000 012	3351.5	E	002 002	4050.0

TABLE 13: Rovibrational Energies of CH_4 Fundamentals for $J = 1$ Relative to the $J = 0$ Zero Point Energy

	ZPE		
	diagonal	coupled	exptl
	10.48	10.47	10.48[a]
$\nu_1(A_1)$	2927.7	2927.8	
$\nu_2(E)$	1544.5	1544.6	1544.0[a]
$\nu_3(F_2)$	3029.9	3028.7	3028.8[b]
		3029.1	3029.3
		3030.3	3030.5
$\nu_4(F_2)$	1321.5	1311.6	1311.4[a]
		1316.4	1316.2
		1326.1	1326.2

[a] Gray, D. L.; Robiette, A. G. *Mol. Phys.* **1979**, *37*, 1901. [b] Tarrago, G.; Dang-Nhu, M.; Poussigue, G.; Geulachvili, G.; Amiot, C. *J. Mol. Spectrosc.* **1975**, *57*, 246.

modes strong Coriolis coupling splits these modes, as is well-known,[17] and the diagonal energies miss this effect. The coupled results do reproduce these splittings in good agreement with experiment.

4. Summary and Conclusions

We presented variational calculations of vibrational energies of CH_4 and four isotopomers using the general code "Multimode" and two modifications of a high-quality ab initio quartic force field attributable to Lee, Martin, and Taylor. The first modification was to replace the stretch displacement coordinates by Morse coordinates. Calculations using this potential were compared with experiment for CH_4 and generally good agreement was found. The potential was subsequently empirically modified to improve agreement with fifty experimental energies up to 9045 cm^{-1} for CH_4. The energies using the adjusted potential agreed with experiment to within an average error of 2.2 cm^{-1}. Vibrational energies for the isotopomers CD_4, CH_3D, CD_3H, and C_2D_2 were calculated using the adjusted potential. Comparisons with experiment showed very good agreement, with average errors in the range 1−2 cm^{-1}.

Rovibrational calculations were presented for CH_4 for $J = 1$. The well-known Coriolis interaction of mode 4 (of F_2 symmetry), and to a much lesser extent of mode 3 (also of F_2 symmetry) was seen, and agreement with experiment for the absolute energies was found to be very good.

As this work was being written up, we became aware of two other efforts to improve the LMT potential, based on perturbation theory.[7,8] It would be interesting to compare the various results and to use these potentials in variational calculations. In addition, a new global potential for CH_4, based on ab initio calculations, has been developed by Marquardt and Quack.[18] It would of course be of interest to use this potential in variational calculations as well.

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