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Vibrational Levels of Methanol Calculated by the Reaction Path Version of MULTIMODE, Using an ab initio, Full-Dimensional Potential[†]

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An accurate potential energy surface has been determined for methanol from ab initio potential data at the CCSD(T) level of theory with an aug-cc-pVTZ basis. The resulting potential function is valid over all twelve vibrational degrees of freedom for all near-equilibrium and torsional configurations. A torsional reaction path has been derived for this potential, from which the low-lying vibrational levels of methanol have been calculated by the reaction path version of MULTIMODE. Comparisons with experiment and other calculations are made.

1. Introduction

Methanol has become a benchmark example for the study of large-amplitude torsional motion, mainly because it is one of the simplest molecules with such internal isomerization over relatively small barriers.[1] An understanding of the interaction of this large-amplitude motion with other normal modes has intrigued spectroscopists for many years and has therefore been the subject of numerous experimental studies (see, for example, refs 2−5 and references therein). From a theoretical standpoint, the prediction of its infrared spectrum presents a real challenge due to the interaction of the torsional motion with both the OH and CH stretching motions, in particular. For the former, the internal torsional barrier is sensitive to the quanta of OH excitation, almost doubling by $n_\nu = 6$;[6] for the latter, the torsional tunnelings of the asymmetric CH fundamentals $\nu = 2$ and $\nu = 9$ are inverted, degenerate *E* levels are lower than nondegenerate *A* levels, whereas those of the symmetric CH fundamental $\nu = 3$ are normal, with *A* levels below *E* levels. There have been several theoretical attempts to clarify the torsional anomalies, mainly those found in refs 1 and 7−9, and a theoretical investigation of the force-field of methanol has been undertaken by Hanninen and Halonen.[10] More recently, Sibert and Castillo-Chara[11] reported a normal-coordinate force-field (up to fourth order) that is a function of the torsional angle for methanol. This force field is based on high quality ab initio calculations as well as some empirical adjustments to improve agreement with experiment. The vibrational energies were obtained with high order perturbation theory.

We have recently carried out initial studies on the vibrational levels of methanol, using a point-wise harmonic density functional theory (DFT) potential and internal coordinate path variational approach.[12] This technique is very similar to that used in ref 9 and is only a slight variation of the more familiar reaction path of Miller et. al.[13] introduced by us for the study of hydrogen peroxide.[14] Our main findings were that the potential energy surface (PES) of methanol could possibly be represented by a global fit in full dimensionality, as the study of its vibrational levels suggested a “well-behaved” set of normal modes orthogonal to the torsional path. This is to say that there was a relatively non-interacting set of 11 normal modes all the way from the minima to the torsional saddle points. Because of the simplicity of the potential used in ref 12, we could say nothing about tunneling irregularities of the type discussed in ref 7, but we were able to confirm that converged calculations of all fundamentals were possible by such a variational approach.

We have had recent experience at generating global potentials for large molecules, using high quality ab initio calculations of energies and fitting them with a polynomial basis that is invariant with respect to all permutations of like atoms. We have used these fits in variational calculations with the variational code MULTIMODE (MM) and, in particular, with its reaction path version (MM-RPH).[15,16] Methanol is of similar size to the molecules studied in these studies ($H_3O_2^-$ and $H_5O_2^+$), and also has high symmetry (permutation-inversion symmetry G_6 which is isomorphous with C_{3v}). We therefore concluded that a more rigorous analysis of methanol was justified, using high-accuracy ab initio methodology in order to generate a semi-global potential energy function in full dimensionality which could then be used in a modified version of MM-RPH which will be outlined later.

The purpose of this work, therefore, is twofold. First, we wish to produce a full-dimensional, semi-global potential energy surface for methanol from high-quality ab initio calculations which could be used for a variety of studies of this benchmark

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system. Second, we wish to test our recent variational scheme MM-RPH on this potential in order to validate the method for such 12-mode systems, paying particular attention to the effect of the interaction of torsion with the remaining normal modes; in so doing, we wish to verify the accuracy of our potential and that it predicts the correct *A*/*E* orderings determined from experiment. As we will see, the convergence of our variational calculations depends on two new developments of the MM-RPH algorithm.

2. Potential Energy Calculations

The methanol potential energy surface is a complete sixth-order polynomial, fit to 19 315 ab initio grid points computed by MOLPRO 2002.6[18] at the coupled cluster singles, doubles, and non-iterative triples correction CCSD(T) levels together with a correlation-consistent polarized valence triple-ζ basis augmented with diffuse functions (aug-cc-pVTZ).

The ab initio data consist of three subsets. First, 6876 geometries were chosen along or close to the torsional path which had previously been optimized at the B3LYP/6-311+g(2df,2pd) level.[12] Of these geometries, 722 were on the path itself (at half-degree intervals), and the remainder corresponded to small oscillations away from the path, where the oscillations were generated from pilot MM-RPH calculations using the potential in ref 12 with two-mode coupling of the potential terms. We assume that the geometry differences between CCSD(T)/aug-cc-pVTZ and B3LYP/6-311+g(2df,2pd) can be considered fairly insignificant for this data subset. The energies of most of these points are found below 500−1,000 cm^{-1} relative to the minimum. Second, 9786 geometries were chosen to have relatively larger and random displacements away from the fully relaxed torsional path. Third, 2653 points were chosen to be even further away from the torsional path. Some of these were selected from spurious negative-energy regions found during initial MM-RPH calculations which used only the first two data sets. Our complete set of 19 315 data points can be summarized as follows. There are 6371 points below 500 cm^{-1}, 9167 points below 3000 cm^{-1}, 10 564 points below 5000 cm^{-1}, 13 269 points below 10 000 cm^{-1}, 16 538 points below 20 000 cm^{-1}, 17 581 points below 25 000 cm^{-1}, and 19 178 points below 110 000 cm^{-1}, and the remaining 137 points are sparsely distributed in the 110 000−750 000 cm^{-1} energy range (all energies are relative to the potential minimum). In practice, only unique data between $\tau = 0$ and $\tau = 60°$ (see Figure 1) are calculated and used in the fit. Because of the permutational invariance of the PES, all other equivalent configurations will be guaranteed to have identical energies. Furthermore, in construction of the reaction path, all of the required properties can be obtained by successive reflections about $\tau = 60°$, $\tau = 120°$, $\tau = 180°$, respectively.

This PES is permutationally invariant and consists of 3338 coefficients. Details of the fitting procedure and polynomial basis haved been given elsewhere[19] and will not be repeated here, except for the following aspects: the auxiliary variables $X_{ij} = \exp(-R_{ij}/3)$ were used as usual, in which R_{ij} are inter-nuclei distances between atom *i* and atom *j*; the weight of each single ab initio point was defined by $0.1/(0.1 + E)$ where *E* is the energy in Hartree relative to the potential minimum. Finally, the 3338 coefficients were determined from the least-squares singular value decomposition (SVD) algorithm, using the DGESVD subroutine in the LAPACK library with the conditioning number set to 1×10^{-11}. The root mean square (rms) fitting error for the whole data set is as small as 14.6 cm^{-1}. Because of the higher density of ab initio data in the low-energy region, the rms errors at the 500, 3000, 5000, 10 000, and 20 000 cm^{-1} cutoffs are 0.5, 1.5, 2.6, 5.3, and 8.4 cm^{-1}, respectively. This verifies the excellent fitting accuracy of our surface.

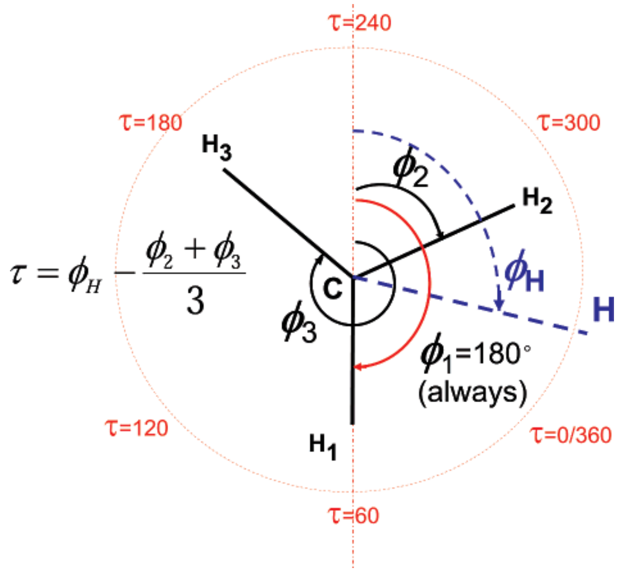

Figure 1. Definition of the torsional angle τ used in this work. Three H atoms, H_1, H_2, and H_3 are bonded with the C atom. The C−O bond is taken as the *z* axis and all atoms are projected onto the *x*−*y* plane (the O atom is not shown). Here, the H_1 atom is taken as reference, and the H_1−C bond is extended to be the reference line. If we take H_2 or H_3 as reference, the corresponding values of τ would differ by $n \times 120$ degrees ($n = 2$ or 3, respectively).

This PES represents version I of a surface that will be extended in the near future to describe dissociation to CH_3 + OH. Here, we validate the accuracy of the PES to describe the vibrational energies of CH_3OH and their tunneling splittings. This PES is available on request.

The torsional angle, τ, should have G_6 symmetry in order to describe the internal rotation of the OH group around the C−O axis. The conventional definition[20] utilized the average of the three dihedral angles H−O−C−H1/2/3; $\tau = (d_1 + d_2 + d_3)/3$, to give the overall torsional magnitude without specifying any reference C−H bond. In this paper, we used the definition of the torsional angle τ given in Figure 1. In our definition, any one of the three C−H bonds can be taken as reference, and the corresponding final τ values would depend on the particular reference bond. The three equivalent torsional angles are thus separated by 120 degrees, for example, 35 degrees, 155 degrees, and 275 degrees. This definition would guarantee that at the potential minimum $\tau = 0/120/240$ degrees and guarantee that at the saddle point (SP) on the torsional path $\tau = 60/180/300$ degrees. The definition of τ in Figure 1 is equivalent to $(d_1 + d_2 + d_3 - \pi)/3$. This makes the reaction path coordinate τ consistent with G_6/C_{3v} symmetry, as required. This has also been noted by Sibert and Castillo-Chara[11] whose coordinate is very similar to ours, although they derived theirs from a coordinate used by Miani et al.[21] in dihedral angles d_n. It is perhaps worth noting that as our PES is fully invariant to interchange of like atoms, it actually transforms as G_8. However, because the reaction path cannot interchange H atoms, only rotate them, our energy levels can at best be specified in the reduced C_{3v} symmetry (which is isomorphous with G_6 symmetry), as has been noted by Hougen.[22]

Using the torsional angle defined above, we have located the fully relaxed torsional path from the fit; that is, at each specific τ value (at half degree intervals), the potential energies are

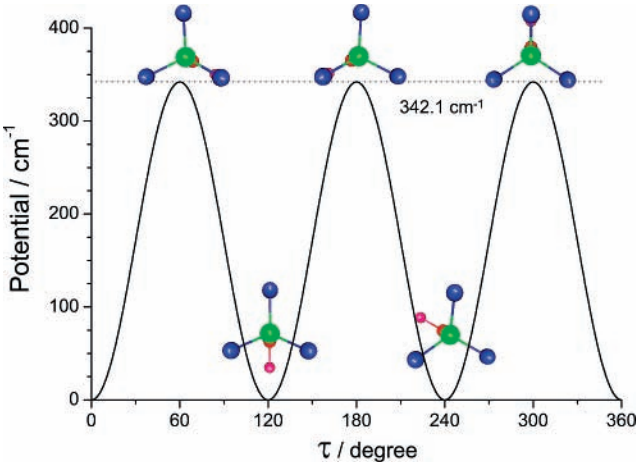

Figure 2. Fully relaxed torsional path of methanol located on the fitted PES. The local minima or maxima are exactly at $n \times 60$ degrees, where n can be any integer.

minimized with repect to all other (11) degrees of freedom. Geometries at the minima and saddle points have perfect C_s symmetry. The original torsional barrier to the SP on the fit is 342.1 cm^{-1}, relative to the minimum, as depicted in Figure 2.

The PES of methanol presented in this paper is the first full-dimensional semi-global PES constructed from wholly ab initio data, and we will demonstrate that it predicts a low-energy spectrum almost comparable with that resulting from a more empirical force field. Also, our method of construction of the PES is completely general and has been applied to a variety of molecules of comparable size ($H_3O_2^-$,[15] $H_5O_2^+$,[15] and $C_2H_3^+$ [17]). The PES presented here is expressed as a function of all of the internuclear distances and is semi-global in these variables. In addition, it is invariant with respect to all permutations of the four H atoms. This contrasts to the potential of Sibert and Castillo-Chara[11] which is expressed as a force field in symmetry coordinates times sine and cosine functions in the torsional angle.

3. MULTIMODE Reaction Path Calculations

Calculations based on the MM-RPH code have been reported recently[12,14−16] so only the relevant details will be discussed in this paper. The main point is that structures along the torsional coordinate discussed above (at half-degree intervals) should form a smoothly varying path. By this, we mean that there should be no abrupt deviations in the derivatives either of the path points themselves or of their associated orthogonal normal coordinate vectors. An excellent example of what is *not* wanted is to be found in our parallel work on malonaldehyde.[12] Here, there is much mixing between normal modes for different regions of the reaction path, which makes it difficult to label the modes uniquely. In methanol, on the other hand, the orthogonal normal modes remain relatively “pure” for all regions of the torsional coordinate, with no signs of any interchange in their ordering throughout the entire path. A full description of how the torsional reaction path is obtained is given in ref 14.

Once the torsional path is established from the potential, we form torsional basis functions in $\cos(m\tau)$ and $\sin(m\tau)$ which are symmetric and antisymmetric, respectively, with respect to reflection in a C_s plane of symmetry. Basis functions in the remaining 11 normal coordinates are harmonic-oscillator functions determined from the values of ω_e at equilibrium. Thereafter, the variational procedure is quite general and does not depend on the nature of the torsional path. All basis functions are optimized via a series of one-dimensional contractions followed by a vibrational self-consistent field (VSCF) calculation, from which the virtual functions for the zero point level are selected. These functions are then used as an expansion set in a vibrational configuration interaction (VCI) calculation using a restricted direct product basis involving (a) discrete mode-coupling, (b) maximum-allowed excitation quanta, and (c) maximum sum-over-quanta.[14,23] This is necessary in order to introduce the dominant terms into the VCI procedure while, at the same time, minimizing the final size of the VCI matrix. Integration of all matrix elements is carried out by numerical Gauss quadrature. For large molecules, it becomes virtually impossible to integrate over all modes simultaneously, and the MM algorithm assumes that by integrating over single modes, two modes, three modes, and so forth to m modes,[23] there will be convergence in the matrix element integration (usually by four-mode or five-mode coupling). It is therefore necessary to test for convergence in the integration by restricting the integration to different m-mode couplings of both potential and Coriolis terms ($m = 2, 3, 4, ...$). It is more conventional, in a normal-mode analysis, to expand the potential about a single reference (as in the MM variant MM-SR). Here, we can express the total potential by $V(Q)$. In MM-RPH, however, there are different expansions of the potential at every τ point, and so we must express the total potential by $V(\tau;Q)$. This implies that all integrals over Q must also be accompanied by integration over τ.[14] Apart from this, however, the algorithms for MM-SR and MM-RPH are identical. In the present work, we found that convergence was reached for a potential coupling of four and a Coriolis coupling of two (which implies five-mode potential and three-mode coriolis coupling as integration is everpresent over the torsional coordinate).

Despite all the steps taken to keep the matrix size to a minimum, there will always come a time when the size increase caused by the number of modes outweighs the savings brought about by our restrictions imposed above on the expansion set. For methanol (12 modes), convergence of all fundamentals can only be achieved for Hamiltonian matrices well in excess of order 100 000, this despite using the symmetry savings of C_s available to us. For example, using maximum quanta of 5 in the 11 modes orthogonal to the path and a total of 5-mode excitation in the VCI basis with 1-mode, 2-mode, 3-mode, 4-mode, 5-mode sums-over-quanta of 5, 10, 15, 12, 10, respectively, we find that the VCI matrix factorizes into two C_s blocks of order 147 537 and 139 524 for a maximum quantum of 26 in the torsional coordinate. Following our initial work on methanol,[12] we anticipated this forthcoming difficulty by introducing a perturbation scheme designed to reduce the size of the Hamiltonian matrix while retaining accuracy in its eigenvalues.[24] Briefly, we assume that the large bulk of information required to reproduce the energies of the fundamentals, first overtones, and combination bands will be present in a matrix comprising solely the one-mode and two-mode excitations. We therefore build this matrix with no restrictions on the two-mode sum-over-quanta (see above). This matrix is diagonalized, and its eigenvectors are stored. The second-order interaction between a user-defined subset of these eigenfunctions and the remaining three-mode, four-mode, and five-mode expansion functions is evaluated, and an expansion function is discarded if no second-order interaction is greater than a user-defined tolerance for *any* of the one- and two-mode eigenfunctions. We found in the present work that a value of this tolerance of 10^{-4} cm^{-1} reduces the two C_s blocks to 100 893 and 97 835, respectively.

TABLE 1: Experimental Vibrational Energy Levels (in cm^{-1}) of $^{12}CH_3OH$ Compared with those Calculated in this Work (MM) and Refs 9 and 11[a]

level	sym	expt	MM	[11]	[9]	expt	MM	[11]	[9]
ν_8	A_1	1033.8[b]	1026.3	1031.0	1064.8	+8.27	+10.50	8.4	+8.4
ν_7	A_1	1074.5[c]	1079.9	1074.0	1129.1	+4.61	+7.62	4.6	−8.4
ν_6	A_1	1335.8[b]	1321.9	1321.0	1408.8		+20.01	23.7	+8.7
ν_5	A_1	1454.5[c]	1446.8	1450.2	1526.6		+8.72	7.6	+8.1
ν_4	A_1	1486.4[c]	1483.8	1484.0	1642.2		−2.72	−5.3	−11.1
ν_3	A_1	2844.2[c]	2839.5	2844.4	3083.3	+9.07	+9.09	5.6	+7.8
ν_2	A_1	2999.0[c]	2986.3	3005.2	3243.4	−3.26	−0.68	−2.8	−3.6
ν_1	A_1	3683.9[b]	3675.0	3680.2	3902.0	+6.30	+6.90	6.5	+7.2
$2\nu_8$	A_1	2054.7[b]	2038.7	2049.7	2129.6	+8.90	+12.85	7.8	+8.6
$2\nu_7$	A_1	2140.6[c]	2152.5	2141.4	2253.4	+2.29	+5.67	1.9	−8.0
$2\nu_6$	A_1	2632.0[b]	2678.4				−26.47		
$\nu_7 + \nu_8$	A_1	2097.3[d]	2097.6	2095.3	2194.7	+4.65	+6.36	4.6	−8.6
ν_{11}	A_2	1164.0[e]	1156.5	1159.9	1242.4	−7.43	−5.42	−7.5	−8.2
ν_{10}	A_2	1481.8[c]	1475.1	1465.0	1631.5		−4.24	−4.7	−11.9
ν_9	A_2	2966.6[c]	2961.5	2956.5	3196.4	−5.48	−3.43	−4.0	−3.2
$\nu_8 + \nu_{12}$	A_2	1231.6[f]	1234.9		1279.5	−76.93	−56.74		−82.6
$\nu_8 + \nu_{11}$	A_2	2190.6[d]	2176.7	2183.6	2307.9	−7.70	−3.19	−8.4	−8.2

[a] Left-hand entries are the nondegenerate A_1 and A_2 levels in the C_{3v} point group arising from the MM A' and A'' levels from calculations in C_s symmetry, respectively. Right-hand entries are the relative energies of the corresponding degenerate E levels in the C_{3v} point group. [b] Reference 5. [c] Reference 2. [d] Reference 27. [e] Reference 28. [f] Reference 29.

TABLE 2: Experimental Torsional Energy Levels (in cm^{-1}) of $^{12}CH_3OH$ Compared with those Calculated in this Work (MM) and Refs 9 and 31[a]

level	C_3v sym	expt	MM	[31]	[9]	C_3v sym	expt	MM	[31]	[9]
0ν	A_1	0.0[b]	0.0	0.0	0.0	E	9.1[b]	8.7	8.8	8.2
1ν	E	208.9[b]	205.3	209.4	216.7	A_2	295.5[b]	267.0	294.5	297.8
2ν	A_1	352.2[b]	388.2	353.2	363.5	E	510.3[b]	509.3	515.5	517.2
3ν	E	751.0[b]	762.3	749.2	758.7	A_2	1046.7[b]	1017.8	1044.1	1057.7
4ν	A_1	1047.6[b]	1078.0	1049.0	1058.1	E	1396.2[c]	1391.0		1413.9

[a] Left-hand entries are the A′ levels arising from the MM calculations in C_s symmetry. Right-hand entries are the A″ levels arising from the MM calculations in C_s symmetry. Individual levels are specified in the C_{3v} point group. [b] Reference 30. [c] Reference 9.

Our diagonalization procedure is a modification of a Davidson-type iteration scheme,[25] in which the half matrix is first stored on disc. Such procedures involve reading information from disc many times, in particular, during the formation of $H_{rs}\cdot\Psi$, where H_{rs} is a Hamiltonian matrix element of the original matrix and Ψ is a trial wavefunction.[23] We now address this problem and improve our diagonalization procedure further by introducing a new user-defined sparsity tolerance such that a matrix element is only written to disc if its absolute value is greater than this tolerance. While this does not decrease the matrix size itself, it can greatly reduce both the computational time and the disc storage, both of which become a problem for very large matrices. We found in the present work that values of 10^{-8} cm^{-1} and 10^{-9} cm^{-1} which define our sparsity tolerance gave identical results, with an approximate overall performance improvement (disc and time) of between 5 and 10%. In fact, by using a combination of both perturbation and sparsity criteria, the convergence of the final energy levels can be more successfully manipulated by the user.

Finally, we have improved our diagonalization scheme by recognizing that many eigenvalues and eigenvectors may be required. Following a suggestion by Kaledin and Bowman,[26] we allow for the possibility of collecting the required eigenvalues and eigenvectors in groups, commencing with the group containing the lowest eigenvalues. This becomes necessary as both the number of required eigenvalues and the number of iterative cycles increase, since the iterative diagonalization scheme involves internal diagonalizations of matrices whose orders can reach the product of these two quantities. This new feature is trivially implemented as it involves only an extra initial Schmidt orthogonalization between the initial-guess eigenvectors[23] of each new group to be processed and the converged eigenvectors of previous groups. In this work, we have found that 1000 eigenvalues can efficiently be collected in two groups.

4. Results and Discussion

The calculations presented earlier in ref 12 were based only on a harmonic DFT potential which can be represented as follows: ($V = V(\tau) + 1/2\Sigma_k\omega_k^2(\tau)Q_k^2$). Although this potential served the purpose of testing our MM-RPH scheme for convergence, it is insufficient in that tunneling anomalies can never be achieved for a PES of this simple harmonic form. Therefore, since it was verified in ref 12 that convergence of all fundamentals was possible, we considered a more complete anharmonic PES to be justified. The work in this paper reports the results for such an anharmonic potential in full dimensionality, derived from high-accuracy ab initio calculations. We have seen that the anharmonic effects impede convergence, and therefore this work also demonstrates new developments during the diagonalization stage of MM calculations which help to overcome this problem. Namely, we have used the various new techniques to diagonalize large matrices that were described above. These techniques were essential in the present study.

The vibrational energy levels of methanol calculated in this work are presented in Tables 1 and 2, where they are compared with experiment and previous calculations.[9,11] Initial calculations indicated that slight improvements could be made to the pure ab initio potential by scaling the normal modes for CH_3 rock and OH stretch by the simple transformation $Q' = 1.01Q$. Also, when compared with the barrier height of 374 cm^{-1} obtained from experiment,[1] our ab initio value was approximately 30 cm^{-1} too low and so we have added a correction term to the pure torsional potential of the form $15(1 - \cos(3\tau))$. The results in Tables 1 and 2 reflect these modifications to the potential.

In Table 1, we give the fundamental wavenumbers and a selection of first-overtones and combination bands for the three components (*A* and *E*) which arise from the 3-fold permutational symmetry group C_{3v}. It can be seen that our results are very satisfactory when compared to experiment and generally superior to those of the earlier calculations in ref 9 which also uses a reaction path Hamiltonian. On the other hand, when compared with the results of the perturbation calculations,[11] our results are slightly inferior. It must be emphasized however that the force field used in ref 11 was optimized somewhat to agree with experiment. It is however encouraging that the present PES does accurately predict the tunneling of the various levels through the 3-fold barrier both with regard to the magnitude of the *A*/*E* splittings and their energy reversals. These seemingly anomalous energy patterns have been discussed at length by Wang and Perry (see ref 7 and references therein) in terms of interactions between the torsional motion and the asymmetry in the CH stretching modes. It appears therefore that our potential energy reproduces these asymmetry features well, although there are systematic errors in the torsional progression, as we shall see next.

Turning to Table 2, we present our calculated results for the pure torsional progressions. Our predicted levels, in particular, the *E* levels, are accurate; however, there are errors in the *A* levels which systematically increase A_1 energies by 30 cm^{-1}, while decreasing the corresponding A_2 energies, again by 30 cm^{-1}. At the moment, we are unsure which asymmetry coupling with torsion is responsible for this error and in what form it should be represented. We will therefore leave this as an outstanding refinement problem to be tackled at some later stage, although it appears to be connected to force constants in the potential of the form $f(Q)\cos(6\tau)$, since terms of this nature have equal and opposite effects on A_1 and A_2 energies. On completion of this work, we were kindly sent hitherto unpublished results arising from the force field in ref 11 and which we have included in Table 2. It can clearly be seen that the correct force constants are present in that force field, which will be of value to us in future work.

Our current version of MM-RPH cannot quite reach the degree of convergence required to calculate other high-energy levels recorded experimentally,[5] because of the sheer sizes of matrices involved. This general problem of large matrix diagonalization is, however, being tackled in a collaboration at the European Supercomputer Centre at CINECA (Bologna, Italy), and we also intend to revisit this aspect of the methanol spectrum at some later stage.

5. Summary and Conclusions

In this paper, we reported accurate calculations of low-lying vibrational energy levels of methanol using purely ab initio techniques. We have calculated and fit 19 315 ab initio energies of CCSD(T) quality for a wide variation of geometrical configurations. We have used this potential in the reaction path version of MULTIMODE (MM-RPH), from which we have been able to calculate fully converged energies to 5000 cm^{-1} relative to a zero point energy of 11 195.82 cm^{-1}. From a comparison with experiment, we have improved the pure ab initio potential slightly by scaling the CH_3 rock and OH stretch normal coordinates Q to $1.01Q$ and by correcting for the barrier height with the addition to the reaction path potential of a correction term $15(1 - \cos(3\tau))$. The resulting energy levels have been compared very favorably with experiment and also compare favorably with previous calculated energies, except for some levels associated with the pure torsional progression in particular, although the fundamentals do exhibit less severe errors. We intend to return to this outstanding problem at a future date with a closer look at the torsional anharmonicity and, in particular, at the interaction between the torsion and the remaining normal modes. We will also attempt to calculate higher-energy levels which are currently prohibitive in MM-RPH.

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