

**Full-dimensional calculations of rovibrational levels of five-atom molecules using two different strategies: Applications to CH<sub>4</sub>, CHD<sub>3</sub>, CH<sub>3</sub>D and CH<sub>3</sub>F**

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Quantum mechanical calculations of ro-vibrational energies of CH<sub>4</sub>, CHD<sub>3</sub>, CH<sub>3</sub>D, and CH<sub>3</sub>F were made with two different numerical approaches. Both use polyspherical coordinates. The computed energy levels agree, confirming the accuracy of the methods. In the first approach, for all the molecules, the coordinates are defined using three Radau vectors for the CH<sub>3</sub> subsystem and a Jacobi vector between the remaining atom and the centre of mass of CH<sub>3</sub>. Euler angles specifying the orientation of a frame attached to CH<sub>3</sub> with respect to a frame attached to the Jacobi vector are used as vibrational coordinates. A direct product potential-optimized discrete variable vibrational basis is used to build a Hamiltonian matrix. Ro-vibrational energies are computed using a re-started Arnoldi eigensolver. In the second approach, the coordinates are the spherical coordinates associated with four Radau vectors or three Radau vectors and a Jacobi vector, the frame is an Eckart frame. Vibrational basis functions are products of contracted stretch and bend functions and eigenvalues are computed with the Lanczos algorithm. For CH<sub>4</sub>, CHD<sub>3</sub>, and CH<sub>3</sub>D, we report the first  $J > 0$  energy levels computed on the Wang-Carrington (WC) potential energy surface [X. G. Wang and T. Carrington, *J. Chem. Phys.* 141, 15 (2014)]. For CH<sub>3</sub>F the PES of Zhao *et al.* [*J. Chem. Phys.* 144, 204302 (2016)] was used. All the results are in good agreement with experimental data.

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## I. INTRODUCTION

Even though methane is a simple five-atom molecule, much effort is still being devoted to the study of its infrared spectroscopy<sup>1-15</sup>. Due to the complexity of their spectra, methane and its isotopologues serve as benchmark systems for theorists developing and testing quantum mechanical methods. A great variety of methods exists, using for example, normal coordinates, perturbation theory, curvilinear coordinates and contracted bases.<sup>15-25</sup>.

In this paper, we compare the results of two approaches for calculating rovibrational energy levels for CH<sub>4</sub>, CHD<sub>3</sub> and CH<sub>3</sub>D, using the Wang-Carrington (WC) potential energy surface (PES)<sup>26</sup>, and for CH<sub>3</sub>F, using the PES of Ref 27.

In a previous paper<sup>27</sup>, quantum mechanical calculations of vibrational energies of methane and fluoromethane were done and very good agreement with previous theoretical results and with experimental data was obtained. In this paper we use similar ideas to compute ro-vibrational levels. We use as vibrational coordinates the polyspherical coordinates (along with Euler angles for the rotation of CH<sub>3</sub>) associated with four vectors: three Radau vectors for the CH<sub>3</sub> subsystem and a Jacobi vector between the remaining atom and the centre of mass of CH<sub>3</sub>. Euler angles specifying the orientation of a frame attached to the CH<sub>3</sub> subsystem with respect to a frame attached to the Jacobi vector are used as additional vibrational coordinates.<sup>27</sup> One term in the kinetic energy operator (KEO) is the Radau ro-vibrational KEO for CH<sub>3</sub>. It has the advantage of being simple. The Radau coordinates are close to valence internal coordinates when the central atom is heavier than the end atoms, which is the case for CH<sub>3</sub>. For YCZ<sub>3</sub> molecules, it is possible to compute ro-vibrational energies without attaching a frame to a subsystem. However, our long-term goal is to study processes in which the bond between Y and CZ<sub>3</sub> breaks, such as the reaction H+CH<sub>4</sub> → H<sub>2</sub>+ CH<sub>3</sub>. In this case, using the subsystem approach is clearly advantageous because coupling between the CH<sub>3</sub> coordinates and the coordinates of the Jacobi vector is weak when H is far from CH<sub>3</sub>. An important goal of this paper is to demonstrate that the subsystem coordinates work well for the purpose of computing ro-vibrational levels of methane and its isotopologues and also CH<sub>3</sub>F. When using the subsystem coordinates, we evaluate DVR matrix-vector products to compute eigenvalues by doing sums sequentially (like in Ref.<sup>28</sup>): only small matrices for each degree of freedom are stored.

As in Ref.<sup>27</sup>, the full basis is a direct product of potential-optimized discrete variable representation (PODVR) functions<sup>29,30</sup> and Wigner functions<sup>31</sup>. Its eigenvalues are computed with the

ARPACK eigensolver<sup>32</sup>. We shall refer to the approach using subsystem coordinates and a direct product basis as the SSDP method. It is limited by the need to store many vectors in memory (as explained above, we never store the full Hamiltonian matrix but only small matrices for each degrees of freedom). A direct product DVR basis has previously been used to compute vibrational energy levels of methane in normal and curvilinear coordinates<sup>33</sup>.

Brocks et al. first proposed attaching axis systems to two subsystems and using the Euler angles that specify their orientation as vibrational coordinates.<sup>34</sup> In the case of  $YCZ_3$  in this paper, one of the two subsystems is a single atom. Wang and Carrington have used a similar subsystem approach to study  $H_2O$ -atom complexes.<sup>35</sup> Gatti has used a subsystem KEO with nonrigid subsystems to compute energy levels of  $NH_3$ <sup>36,37</sup>. In Ref. 35, the coordinates are three vibrational coordinates for  $H_2O$ , three Euler angles that specify the orientation of  $H_2O$  and two Euler angles for the overall rotation. These are good coordinates because coordinates of different sub-systems are weakly coupled. Subsystem KEOs with rigid or adiabatically constrained subsystems have been used for several molecules, e.g. ammonia dimer and water dimer<sup>38-41</sup>.

We compare energies for  $CH_4$  computed with the SSDP method with those obtained from a KEO in terms of the polyspherical coordinates associated with four Radau vectors (no subsystem). For  $CHD_3$  and  $CH_3D$ , we use the polyspherical coordinates associated with three Radau vectors and a Jacobi vector (no subsystem). When it is written in terms of angular momentum operators, the KEO is simple, if the molecule-fixed frame is chosen in the standard way. See references<sup>19,42</sup> and Sec. 3.2.2 (i) of Ref.<sup>43</sup>. It is worth noting that the KEO has exactly the same expression in full Radau (four Radau vectors) or mixed Jacobi/Radau (one Jacobi vector and four Radau vectors): only the masses differ and the physical meaning of the coordinates but the analytical expression is the same: see the discussions in the appendix of Ref 28 and in Sec. 3.2.2 (i) of Ref.<sup>43</sup>. When using the polyspherical coordinates associated with four Radau vectors or three Radau vectors and a Jacobi vector, we use an Eckart frame that minimizes the Coriolis coupling and a contracted basis. In this paper we call this the Numerical Eckart KEO Contracted Basis (NEKCB) method. It is presented in detail in Ref. 23. This method allows one to converge more levels than the SSDP method because it does not require storing many vectors or even the potential on full-dimensional grid. In this paper, it is used to calibrate the SSDP method.

## II. THE ROTATIONAL KINETIC ENERGY OPERATOR FOR MIXED JACOBI/RADAU COORDINATES

In this section, we present the KEO used in the SSDP method. As in Ref. 27, we use for, all YCZ<sub>3</sub> molecules, a Jacobi vector and three Radau vectors as depicted in Fig. 1 of Ref. 27. The Radau vectors,  $\vec{R}_i$  ( $i = 1, 2, 3$ ), are vectors  $\overrightarrow{AZ}_i$ , from A the “canonical” point of CZ<sub>3</sub> (see Fig. 1 of Ref. 27), to the three Z atoms. If we define  $\vec{r}_i = \overrightarrow{G_{CZ_3}Z_i}$  ( $i = 1, 2, 3$ ) with  $G_{CZ_3}$  the center of mass of CZ<sub>3</sub>, the three Radau vectors are

$$\begin{aligned}\vec{R}_1 &= (1 - \alpha m_{Z_1})\vec{r}_1 - \alpha m_{Z_2}\vec{r}_2 - \alpha m_{Z_3}\vec{r}_3 \\ \vec{R}_2 &= -\alpha m_{Z_1}\vec{r}_1 + (1 - \alpha m_{Z_2})\vec{r}_2 - \alpha m_{Z_3}\vec{r}_3 \\ \vec{R}_3 &= -\alpha m_{Z_1}\vec{r}_1 - \alpha m_{Z_2}\vec{r}_2 + (1 - \alpha m_{Z_3})\vec{r}_3,\end{aligned}\tag{1}$$

where

$$\alpha = (1 - \sqrt{\frac{M}{m_C}})/m_{Z_{1,2,3}},\tag{2}$$

and  $m_{Z_{1,2,3}} = m_{Z_1} + m_{Z_2} + m_{Z_3}$ ,  $M = m_C + m_{Z_{1,2,3}}$ . The Jacobi vector is from the center of mass of CZ<sub>3</sub> to the Y-atom, (see Fig. 1 of Ref. 27),  $\vec{R}$ .

The full set of coordinates used in the SSDP method is:  $\alpha, \beta, \gamma, u_1 = \cos \theta_1, u_2 = \cos \theta_2, \varphi_1, R_1, R_2, R_3, \beta_s, \gamma_s, R$ .  $\theta_1, \theta_2, \varphi_1, R_1, R_2, R_3$  are the usual vibrational polyspherical coordinates for CZ<sub>3</sub>.  $\beta_s$  and  $\gamma_s$  are Euler angles that specify the orientation of a frame attached to CZ<sub>3</sub> with respect to a frame attached to the Jacobi vector and are additional vibrational coordinates. Another set of Euler angles,  $\alpha, \beta, \gamma$ , describes rotation. In total there are five Euler angles. One can think of three of them,  $\alpha_s = \gamma, \beta_s$  and  $\gamma_s$  as being internal angles that specify the orientation of the CZ<sub>3</sub> frame with respect to a frame attached to the Jacobi vector whose orientation is determined by only two angles,  $\alpha, \beta$ .<sup>35</sup> Alternatively, one can think of three Euler angles (rather than two),  $\alpha, \beta, \gamma$  as describing rotation of the full molecule and use two (rather than three) as additional vibrational coordinates for CZ<sub>3</sub>.  $R$  is the length of the Jacobi vector. The exact definition of the frame attached to CZ<sub>3</sub> is given in Section II of Ref. 27. The body-fixed (BF) frame used for overall rotation is chosen as follows: its origin is the center of mass of YCZ<sub>3</sub>;  $z^{BF}$  axis is parallel to  $\vec{R}$ ; the  $x^{BF}$  axis is in the plane containing  $\vec{R}$  and  $\vec{R}_3$ . As explained in the introduction, using subsystems has the advantage that the internal Euler angles and vibrational coordinates of different subsystems are weakly coupled with each other when the subsystems are far apart.

To obtain the KEO, we do not derive the operator using the “chain rule”, instead we follow the general rules of the polyspherical approach<sup>43,44</sup>. Polyspherical KEOs can always be written as

a sum of products of one-dimensional operators. This property is advantageous if one solves the Schrödinger equation with the Multi-Configuration Time-Dependent Hartree<sup>45–47</sup> or the Reduced Rank Block Power Method<sup>48</sup> methods. It avoids the need to compute full-dimensional integrals. When Wigner functions are used as basis functions for the internal Euler angles, it is possible to write the KEO in terms of angular momentum operators and apply them directly to the basis. Because in this paper we use a PODVR basis for *all* of the vibrational coordinates, including the internal Euler angles, it is necessary to write the KEO in terms of derivatives with respect to the internal Euler angles. It is singular at  $\beta_s = 0$  or  $\pi$ .

In the polyspherical approach, the KEO is written (we take  $\hbar = 1$ ):

$$2T = -\frac{1}{\mu_R} \frac{\partial^2}{\partial R^2} + \frac{(\vec{J}^\dagger - \vec{L}_{\text{CZ}_{1,2,3}}^\dagger) \cdot (\vec{J} - \vec{L}_{\text{CZ}_{1,2,3}})}{\mu_R R^2} + 2T_{\text{CZ}_{1,2,3}}, \quad (3)$$

where  $\vec{J}$  is the total angular momentum of the system,  $\vec{L}_{\text{CZ}_{1,2,3}}$  is the angular momentum of CZ<sub>3</sub>, and  $\mu_R = \frac{Mm_Y}{M+m_Y}$ ,  $m_Y$  being the mass of the Y atom.  $T_{\text{CZ}_{1,2,3}}$  is the KEO for CZ<sub>1,2,3</sub>. This KEO can be divided into two parts:

$$T = T_{\text{rot}} + T_{\text{vib}}, \quad (4)$$

with  $T_{\text{vib}}$  the “vibrational” part of the KEO that is simply the KEO when  $\vec{J} = \vec{0}$ , and  $T_{\text{rot}}$  the “rotational” part of the KEO. Here, we give only  $T_{\text{rot}}$  since  $T_{\text{vib}}$  is given in the Appendix of Ref. 27,

$$\begin{aligned} 2T_{\text{rot}} = & \frac{1}{\mu_R R^2} \left( \vec{J}^2 + \frac{J_z^2}{\sin^2 \beta_s} + 2i \frac{J_z \cot \beta_s}{\sin \beta_s} \frac{\partial}{\partial \gamma_s} + \cot \beta_s (J_z J_x + J_x J_z) + 2i \frac{J_z}{\sin \beta_s} \frac{\partial}{\partial \gamma_s} \right. \\ & \left. - i J_y \left( \sin \beta_s \frac{\partial}{\partial u_{\beta_s}} + \frac{\partial}{\partial u_{\beta_s}} \sin \beta_s \right) - 2J_z^2 \right) \\ & + \frac{1}{\mu_3 R_3^2} \left( \frac{J_z^2}{\sin^2 \beta_s} + 2i \frac{J_z \cot \beta_s}{\sin \beta_s} \frac{\partial}{\partial \gamma_s} + i \frac{J_z \cot \theta_2}{\sin \beta_s} \left( \frac{\partial}{\partial \gamma_s} \cos \gamma_s + \cos \gamma_s \frac{\partial}{\partial \gamma_s} \right) \right) \\ & - i \frac{J_z}{\sin \beta_s \mu_3 R_3^2} \left( (\sin(\gamma_s + \varphi_1) (v_1 \frac{\partial}{\partial u_1} + \frac{\partial}{\partial u_1} v_1) + \sin \gamma_s (v_2 \frac{\partial}{\partial u_2} + \frac{\partial}{\partial u_2} v_2) + 2 \cos \gamma_s \cot \theta_2 \frac{\partial}{\partial \varphi_1} \right. \\ & \left. + \sin \gamma_s \cot \theta_1 (\sin \varphi_1 \frac{\partial}{\partial \varphi_1} + \frac{\partial}{\partial \varphi_1} \sin \varphi_1) - \cos \gamma_s \cot \theta_1 (\cos \varphi_1 \frac{\partial}{\partial \varphi_1} + \frac{\partial}{\partial \varphi_1} \cos \varphi_1) \right), \end{aligned} \quad (5)$$

where  $J_x$ ,  $J_y$ , and  $J_z$  are the projections of  $\vec{J}$  onto the Body-Fixed axes,  $x$ ,  $y$ , and  $z$ , respectively.  $\mu_3 = m_{Z_3}$  is the mass associated with the third Radau vector.  $\mu_R$  is the reduced mass for the

Jacobi vector. When using a DVR it is important to write the KEO so that it is written in terms of products of explicitly Hermitian and anti-Hermitian one-dimensional operators.<sup>12,28,49</sup> In our method we use PODVR functions as the basis set for each vibrational degree of freedom and the PODVR functions is different according to the different one-dimension hamiltonian.

The last term has been compared with the result obtained with the TANA program<sup>50</sup> for an additional test.

### III. RESULTS

#### A. Calculation of $J > 0$ levels using the PODVR method

In the SSDP method, we use, as in Ref. 27, a direct product PODVR vibrational basis. Each PODVR function is a linear combination of sine DVR functions<sup>51,52</sup>. The strategy is described in Section III of Ref. 27. Table I gives the basis parameters. The range and size of the PODVR basis is the same for  $R_1, R_2, R_3$  and for  $\theta_1, \theta_2$ . Levels that we deem converged are reported in Tables II, III, and IV. To limit the size of the tables, we report only values for  $J = 1, 3, 5,$  and  $10$  for the ground state (Table III for  $\text{CH}_3\text{D}$  and Table VI for  $\text{CHD}_3$ ) and  $J = 1$  levels of higher vibrational states (Table V for  $\text{CH}_3\text{D}$  and Table VII for  $\text{CHD}_3$ ). Our main goal is to calibrate the SSDP and, for this purpose, we do not need all values of  $J$ .

Table II gives eigenvalues for the  $J = 1-5$  rotational excited states of  $\text{CH}_4$ , all associated with the ground vibrational state, computed using the WC PES of Ref. 26 and basis set I of Table I. The comparison with the experimental values shows the high quality of the PES: the energy differences are all smaller than  $0.02 \text{ cm}^{-1}$  and the corresponding relative errors are smaller than  $0.03\%$ . Levels that ought to be degenerate are split because the basis is not symmetrized. The splitting is a measure of the convergence of the calculation and shown as  $\pm$  in column three.

Table III reports the  $J = 1,3,5,10$  rotational excited states of  $\text{CH}_3\text{D}$  using the same PES and basis set III of Table I. In Table IV, we give  $J = 1,3,5$  levels of the same molecule on the same PES but with basis set I (which is larger) of Table I. The levels for  $J = 6-10$  could not be obtained with basis set I because the matrix was too large. We clearly see the limits of the approach and the comparison between the two tables gives a clear indication of the level of convergence of the calculations. We can also converge  $J = 1$  levels of excited vibrational states: they are given in Table V.

We also report in Table VI the eigenvalues for the  $J = 1,3,5,10$  rotational excited states of  $\text{CHD}_3$  using the same PES and basis set III of Table I. For this molecule, we can go to higher values of  $J$ , although the basis set is smaller. This is due to the fact that  $\text{CHD}_3$  is easier to converge than  $\text{CH}_4$  ( $\text{CH}_4$  is more affected by strong Fermi resonances than  $\text{CHD}_3$ ). This is the reason why, with the SSDP method, we can also converge excited vibrational states with  $J = 1$ : they are given in Table VII. The latter were obtained with basis set I of Table I. Again, the comparison with the experimental values is very good.

Finally, we have also calculated the rotational levels of fluoromethane with basis set IV of Table I. We used the PES reported in Ref. 27 and calculated rotational levels of  $\text{CH}_3\text{F}$  up to  $J = 5$ : Table VIII gives the energies and also those reported in Ref 53. Our results have relative errors, with respect to experiment, smaller than 0.27% which is rather small but a little bit larger than the relative error of the results of Ref. 53. The difference between our energies and those of Ref. 53 is due to the fact that we do not use the same PES.

The full wave function is expanded in terms of products of PODVR functions and Wigner functions. The number of vibrational functions is 40353607, 51883209, 10077696, and 10077696 for  $\text{CH}_4$ ,  $\text{CHD}_3$ ,  $\text{CH}_3\text{D}$  and  $\text{CH}_3\text{F}$ , respectively. We use openmp and the intel mkl processor. We evaluate matrix-vector products term by term. For each term, we parallelize over  $K$  and DVR indices that are not coupled by the term. The computer used for these calculations has 20 Inter(R) Xeon(R) 2.60GHz cores and 384 GB memory. The time needed for each calculation depends on the basis size. We store about three times as many Arnoldi vectors as the number of computed eigenvalues. For  $\text{CH}_3\text{D}$  for instance, the calculation with  $J = 5$  (Table III) takes 74 hours and needs 205.384 GB. The calculation of the excited vibrational states with  $J = 1$  for the same molecule (Table VII) takes 51.65 hours and needs 233.045 GB. The calculation is parallelized (OpenMP) using 20 cores.

## B. Calculation of $J > 0$ levels using the NEKCB method

In the NEKCB method, an Eckart frame is used to minimize the Coriolis coupling near the equilibrium geometry. Another important advantage is the contracted basis set. Each basis function is a product of a parity adapted vibrational eigenfunction and a parity adapted Wigner rotational function. Vibrational eigenfunctions are denoted  $|v\rangle$  and Wigner functions are denoted  $|JK\rangle$ . The

$|v\rangle$  are computed with a basis of products of contracted bend and stretch functions  $|bs\rangle$ . The Eckart KEO is computed numerically. See Ref. 23 for details.

If the number of  $|v\rangle$  is large enough that it is possible to compute rotational states for many excited vibrational levels then the NEKCB method is costly. This cost is mitigated by parallelizing the calculation of matrix elements of  $G_{rr}$  and  $G_{rv}P$  in the  $|v\rangle$  basis with MPI, where  $G_{rr}$  and  $G_{rv}$  are rotational and rotational-vibrational Wilson G-matrix elements. The parallelization efficiency is very high because the computations for each MPI process are almost independent. See Ref. 23 for details. Each of the 33 G-matrix integrals in  $|v\rangle$  basis is computed with the  $\mathbf{F}$  matrix idea<sup>13,54,55</sup> used to compute the potential integral in the same basis. These 33 G-matrix ( $G_{rr}$  and  $G_{rv}$ ) integrals are called  $\mathcal{F}$ , corresponding to the  $\mathbf{F}$  matrix one has when integrating the potential.

The basis sets parameters for the NEKCB calculations are given in Tables IX and X. For CH<sub>3</sub>D, the b2s1 basis (also defined in Table III of Ref. 24) is used to compute  $|v\rangle$ . This basis has  $N_b = 962$  contracted bend functions. The efficiency of the parallelization of the calculation of the  $\mathcal{F}$  matrices is nearly 100 % parallelization. Each matrix is divided into blocks labelled by bend functions. With 121 MPI processes, it takes 97 h to compute the  $\mathcal{F}$  matrix for  $N_b = 962$ .  $N_{vib} = 1589$  vibrational wavefunctions, with a cutoff energy  $E_v^{\text{cut}} = 9000 \text{ cm}^{-1}$ , are used to produce the final  $J > 0$  levels of CH<sub>3</sub>D. This basis is denoted b2s1v2 in Table IX. To access the convergence error, we also did calculations with a smaller basis defined by  $N_{vib} = 878$  and  $E_v^{\text{cut}} = 8000 \text{ cm}^{-1}$ , denoted b2s1v1 in Table IX. Energy level differences are smaller than  $0.001 \text{ cm}^{-1}$  for the  $J = 10$  ground state. Another measure of the convergence error is provided by the splitting between two components of the  $E$  levels. This splitting is, for example, smaller than  $0.002 \text{ cm}^{-1}$  for  $J = 1$  levels near  $1500 \text{ cm}^{-1}$ .

A larger primitive bend basis is used for CHD<sub>3</sub> ( $l_x = 35$ ) than for CH<sub>3</sub>D ( $l_x = 29$ ), because the density of bending states of CHD<sub>3</sub> is higher. This basis is necessary if one wishes to converge CH bending states in both molecules to a similar accuracy.<sup>22</sup> The number of contracted bend functions ( $N_b = 989$ ) used to compute  $J > 0$  levels is smaller than that ( $N_b = 1599$ ) used to compute  $J = 0$  levels in Ref. 26. All the  $J > 0$  levels of CHD<sub>3</sub> presented in this paper are obtained with  $N_{vib} = 1833$  vibrational wavefunctions and a cutoff energy  $E_v^{\text{cut}} = 8000 \text{ cm}^{-1}$ , denoted b0s1v1 in Table X. This is fewer than the number in the b1 basis defined in Table IV of Ref. 24, which converged vibrational levels to better than  $0.01 \text{ cm}^{-1}$ . No further convergence tests are performed.

To do the calculations of this paper, we use the symmetry adapted Lanczos method (SAL)<sup>56-59</sup> to simultaneously calculate, for each parity, levels that transform like the two irreducible repre-

sentations of  $C_s$ . In Ref. 23, we exploited only the parity symmetry. Now, having  $C_s$  labels, we are able to assign  $C_{3v}$  or  $T_d$  symmetry labels to the rotational levels.  $C_{3v}$  or  $T_d$  symmetry labels are obtained by using the correlation table between the  $C_{3v}$  or  $T_d$  group and  $C_s$  group<sup>19</sup>. The  $C_s$  group is isomorphic to the permutation-inversion group  $\{E,(12)\}$  where (12) permutes two H atoms. To use the SAL we must apply  $C_s$  projection operators. This in turn requires knowing how the Eckart frame is affected by the  $C_s$  operations. Details will be presented later. Implementation of  $C_s$  symmetry allows us to assign  $A_1$ ,  $A_2$  and  $E$  labels to all the levels of  $\text{CH}_3\text{D}$  and  $\text{CHD}_3$ . Without symmetry labels, one can distinguish non-degenerate and degenerate levels if they are well converged. For instance, one can distinguish between  $A_1$  or  $A_2$  levels and  $E$  levels of  $C_{3v}$  molecules, but one can not distinguish  $A_1$  and  $A_2$  levels and therefore can not compare with the experimental  $A_1/A_2$  levels. Because of the high accuracy of the WC PES, we find that some experimental  $J = 1$  levels of  $\text{CHD}_3$  may be mis-assigned. For example, the experimental  $J = 1(A_2)$  level of the  $2\nu_6(A_1)$  band at  $2073.96\text{ cm}^{-1}$  is noticeably different from the calculated level at  $2067.19\text{ cm}^{-1}$  by  $6.77\text{ cm}^{-1}$ . It is noted that the analysis of all the bands between  $1850$  to  $2450\text{ cm}^{-1}$  by Ulenikov *et al.*<sup>60</sup> is preliminary due to strong perturbations and no successful fit to an effective Hamiltonian has yet been achieved. The same discrepancy was observed in an earlier exact calculation, although it used a less accurate PES (See Table VIII of Ref. 22). We are certain that our calculated levels are accurate and will be helpful in future fits of experimental levels with effective Hamiltonians.

### C. Discussion

Table II gives differences between the eigenvalues obtained with the two theoretical approaches for  $\text{CH}_4$ . For the low-lying levels, the energy differences are smaller than  $0.02\text{ cm}^{-1}$ . Higher in energy, the differences are smaller than  $0.04\text{ cm}^{-1}$ . This proves that both methods work well for computing bound states of methane-like molecules and, in particular, that the KEO of section II is correctly implemented. Energy level differences are probably due incomplete convergence in the SSDP calculations.

We observe the same trend for  $\text{CH}_3\text{D}$  and  $\text{CHD}_3$ . Differences between the two methods for the rotational levels of the vibrational ground state are given in Tables III ( $\text{CH}_3\text{D}$ ) and VI ( $\text{CHD}_3$ ). The differences are very small for low  $J$  levels and increase to no more than  $0.68\text{ cm}^{-1}$  for levels up to  $J = 10$ . Tables V ( $\text{CH}_3\text{D}$ ) and VII ( $\text{CHD}_3$ ) give differences between the NEKCB and SSDP

levels for some excited vibrational states. The difference is larger for some eigenstates but always smaller than  $4 \text{ cm}^{-1}$ . Again, it seems likely that the SSDP calculations are not fully converged.

#### IV. CONCLUSION

We have added rotation to SSDP method of Ref. 27 for  $\text{YCZ}_3$  molecules, which previously was used only for vibrational levels. It uses three Radau vectors and one Jacobi vector and vibrational coordinates defined by attaching a frame to  $\text{CZ}_3$ . We have derived and implemented the corresponding KEO. The method was used to accurately compute eigenstates of  $\text{CH}_4$ ,  $\text{CHD}_3$ ,  $\text{CH}_3\text{D}$ , and  $\text{FCH}_3$ . A large direct product PODVR basis is used and eigenvalues are computed using ARPACK.

This new version of the SSDP method is compared with the more sophisticated Numerical Eckart KEO Contracted Basis (NEKCB) method of Wang and Carrington<sup>23</sup>, which uses a multi-dimensional contraction scheme and an Eckart frame. This Eckart advantage is most important for computing rovibrational eigenstates of molecules whose PES has a single well. In this paper we used the NEKCB to compute new levels for  $\text{CH}_4$ ,  $\text{CHD}_3$  and  $\text{CH}_3\text{D}$ .

The results prove the high quality of the WC PES for  $\text{CH}_4$ ,  $\text{CHD}_3$  and  $\text{CH}_3\text{D}$  and of the PES of Ref. 27 for  $\text{FCH}_3$ . The agreement between the two methods guarantees that the two approaches are accurate and that the new KEO has been correctly implemented. The NEKCB method is more accurate for the calculation of rovibrational eigenvalues and allows us to calibrate the SSDP method, which might be used in the future for reactive scattering.

#### ACKNOWLEDGMENTS

The project was supported by the National Natural Science Foundation of China (21433009, 201703243), The Ministry of Science and Technology of China (2013CB834601), the Chinese Academy of Sciences, and the Natural Sciences Engineering Research Council of Canada. F.G. thanks “French Chinese Network in Theoretical Chemistry” (GDRI 0808) for financial support and D. Lauvergnat for having calculated the KEO with the TANA program for an additional test. T.C. thanks the Alexander von Humboldt Society for support and the Manthe group for hospitality. Jun. Chen. is thankful for the support of China Postdoctoral Science Foundation (Grant No. 2016M600500) and National Postdoctoral Program for Innovative Talents.

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TABLE I. Parameters for the different basis sets used in the SSDP calculations. EG refers to the value of the coordinates at the equilibrium geometry and RANGE to the grid range for coordinate. R,  $R_1$ ,  $R_2$ ,  $R_3$  are in Bohr,  $\theta_1$ ,  $\theta_2$ ,  $\varphi$ ,  $\beta_s$ ,  $\gamma_s$  in radians. PODVR is the number PODVR grid points.

Basis set		$R_1, R_2, R_3$	$\theta_1, \theta_2$	$\varphi$	$\beta_s$	$\gamma_s$	R
I	EG	2.0327	1.9432	4.1036	1.8769	1.0898	2.1936
	RANGE	[1.0,4.0]	[0.87,3.14]	[2.79,5.41]	[0.96,3.14]	[0.0,2.09]	[1.0,4.0]
	PODVR	7	7	7	7	7	7
II	EG	2.0327	1.9432	4.1036	1.8769	1.0898	2.1936
	RANGE	[1.0,4.0]	[0.87,3.14]	[2.79,5.41]	[0.96,3.14]	[0.0,2.09]	[1.0,4.0]
	PODVR	7	7	9	7	7	7
III	EG	2.0327	1.9432	4.1036	1.8769	1.0898	2.1936
	RANGE	[1.0,4.0]	[0.87,3.14]	[2.79,5.41]	[0.96,3.14]	[0.0,2.09]	[1.0,4.0]
	PODVR	6	6	6	6	6	6
IV	EG	2.0361	1.9538	4.0728	1.8651	1.1052	2.7489
	RANGE	[1.0,4.0]	[0.87,3.14]	[2.79,5.41]	[0.96,3.14]	[0.0,2.09]	[1.0,4.0]
	PODVR	6	6	6	6	6	6

TABLE II. Experimental and calculated rotational energy levels of CH<sub>4</sub> (in cm<sup>-1</sup>). First column: the labels of the eigenstates with the format “(J,K) symmetry”, second column: experimental values<sup>61</sup>, third column: results with the SSDP method using the WC PES of Ref. 26, fourth column: the difference between the SSDP energies and the experimental values, fifth column: results with the NEKCB method on the same PES, sixth column: the difference between the NEKCB energies and the experimental values, seventh column: the difference between the SSDP and NEKCB energies.

State	Exp.	SSDP	SSDP-Exp.	NEKCB	NEKCB-Exp.	SSDP-NEKCB
(1,1)F <sub>1</sub>	10.482	10.480 ± 0.001	-0.002	10.479	-0.002	0.001
(3,1)F <sub>1</sub>	62.876	62.864 ± 0.001	-0.012	62.861	-0.014	0.002
(3,1)F <sub>2</sub>	62.877	62.870 ± 0.004	-0.007	62.862	-0.014	0.007
(3,1)A <sub>2</sub>	62.878	62.875	-0.003	62.864	-0.014	0.011
(5,1)F <sub>1</sub>	157.124	157.094 ± 0.002	-0.030	157.088	-0.036	0.006
(5,1)F <sub>2</sub>	157.128	157.102 ± 0.005	-0.026	157.092	-0.036	0.010
(5,1)E	157.137	157.115 ± 0.008	-0.023	157.101	-0.036	0.013
(5,2)F <sub>2</sub>	157.139	157.137 ± 0.014	-0.002	157.103	-0.036	0.034

TABLE III. Experimental and calculated rotational energy levels of CH<sub>3</sub>D (in cm<sup>-1</sup>). The columns are as in Table II. The experimental values are from Ref. 66

State	Exp.	SSDP	SSDP-Exp.	NEKCB	NEKCB-Exp.	NEKCB-SSDP
(1,0)A <sub>2</sub>	7.760	7.759	-0.015	7.758	-0.002	-0.001
(1,1)E	9.131	9.130 ± 0.001	-0.007	9.129	-0.002	-0.001
(3,0)A <sub>2</sub>	46.555	46.553	-0.004	46.544	-0.011	-0.009
(3,1)E	47.924	47.923 ± 0.011	-0.001	47.913	-0.011	-0.011
(3,2)E	52.032	52.033 ± 0.000	0.001	52.021	-0.011	-0.012
(3,3)A <sub>1</sub>	58.883	58.885	0.002	58.871	-0.012	-0.014
(3,3)A <sub>2</sub>	58.883	58.885	0.002	58.871	-0.012	-0.014
(5,0)A <sub>2</sub>	116.358	116.361	0.003	116.331	-0.027	-0.030
(5,1)E	117.725	117.730 ± 0.036	0.004	117.698	-0.027	-0.032
(5,2)E	121.827	121.835 ± 0.002	0.007	121.800	-0.027	-0.035
(5,3)A <sub>1</sub>	128.666	128.678	0.012	128.638	-0.028	-0.040
(5,3)A <sub>2</sub>	128.666	128.679	0.013	128.638	-0.028	-0.041
(5,4)E	138.248	138.262 ± 0.000	0.014	138.219	-0.029	-0.043
(5,5)E	150.579	150.590 ± 0.000	0.011	150.549	-0.030	-0.041
(10,0)A <sub>2</sub>	426.186	426.355	0.169	426.087	-0.099	-0.268
(10,1)E	427.543	427.742 ± 0.378	0.198	427.444	-0.099	-0.298
(10,2)E	431.615	431.858 ± 0.092	0.243	431.515	-0.100	-0.343
(10,3)A <sub>1</sub>	438.404	438.678	0.274	438.304	-0.100	-0.374
(10,3)A <sub>2</sub>	438.405	438.697	0.292	438.304	-0.101	-0.393
(10,4)E	447.916	448.251 ± 0.001	0.335	447.815	-0.101	-0.436
(10,5)E	460.157	460.545 ± 0.000	0.388	460.055	-0.102	-0.490
(10,6)E	475.135	475.565 ± 0.000	0.430	475.031	-0.104	-0.534
(10,7)E	492.860	493.309 ± 0.000	0.449	492.755	-0.105	-0.554
(10,8)E	513.346	513.775 ± 0.000	0.429	513.238	-0.108	-0.537
(10,9)E	536.605	536.959 ± 0.000	0.354	536.495	-0.110	-0.464
(10,10)E	562.654	562.864 ± 0.000	0.210	562.541	-0.113	-0.323

TABLE IV. A comparison of some experimental levels (in  $\text{cm}^{-1}$ ) of  $\text{CH}_3\text{D}$  and SSDP levels computed with a larger basis set than in Table III. First column: the labels of the eigenstates with the format “(J,K) symmetry”, second column: experimental values<sup>66</sup>, third column: SSDP results, using the WC PES of Ref. 26, fourth column: the difference between the SSDP energies and the experimental values, fifth column: the relative error of the SSDP energies.

State	Exp.	SSDP	SSDP -Exp.	Error(%)
(1,0)A <sub>2</sub>	7.760	7.759	-0.001	-0.015
(1,1)E	9.131	9.130 $\pm$ 0.001	-0.001	-0.012
(3,0)A <sub>2</sub>	46.555	46.548	-0.007	-0.014
(3,1)E	47.924	47.917 $\pm$ 0.003	-0.007	-0.014
(3,2)E	52.032	52.026 $\pm$ 0.000	-0.006	-0.012
(3,3)A <sub>1</sub>	58.883	58.877	-0.006	-0.010
(3,3)A <sub>2</sub>	58.883	58.877	-0.006	-0.010
(5,0)A <sub>2</sub>	116.358	116.343	-0.015	-0.013
(5,1)E	117.725	117.711 $\pm$ 0.011	-0.015	-0.013
(5,2)E	121.827	121.814 $\pm$ 0.001	-0.014	-0.011
(5,3)A <sub>1</sub>	128.666	128.654	-0.012	-0.010
(5,3)A <sub>2</sub>	128.666	128.654	-0.012	-0.010
(5,4)E	138.248	138.237 $\pm$ 0.000	-0.011	-0.008
(5,5)E	150.579	150.567 $\pm$ 0.000	-0.012	-0.008

TABLE V. Some  $J = 1$  experimental and calculated rotational energy levels of  $\text{CH}_3\text{D}$  (in  $\text{cm}^{-1}$ ). The columns are as in Table IV. Experimental values are taken from Ref.<sup>60,63–65</sup>

Vib	(K)Sym	Exp.	SSDP	SSDP-Exp.	NEKCB	NEKCB-Exp.	NEKCB-SSDP
(000000)A <sub>1</sub>	(0)A <sub>2</sub>	7.76	7.72	-0.04	7.76	0.00	0.04
(000000)A <sub>1</sub>	(1)E	9.13	9.09 ± 0.00	-0.04	9.13	0.00	0.04
(000001)E	(1)A <sub>2</sub>	1163.91	1164.01	0.10	1163.56	-0.35	-0.45
(000001)E	(1)A <sub>1</sub>	1164.05	1164.14	0.09	1163.70	-0.35	-0.45
(000001)E	(0)E	1168.77	1168.87 ± 0.74	0.10	1168.40	-0.37	-0.47
(000001)E	(1)E	1176.42	1176.54 ± 0.00	0.12	1176.05	-0.37	-0.49
(001000)A <sub>1</sub>	(0)A <sub>2</sub>	1314.42	1314.14	-0.28	1313.96	-0.46	-0.18
(001000)A <sub>1</sub>	(1)E	1315.90	1315.63 ± 0.00	-0.27	1315.45	-0.45	-0.18
(000010)E	(1)E	1478.48	1478.65 ± 0.00	0.17	1478.58	0.10	-0.07
(000010)E	(0)E	1479.96	1480.14 ± 0.18	0.18	1480.07	0.11	-0.07
(000010)E	(1)A <sub>1</sub>	1483.83	1484.02	0.19	1483.95	0.12	-0.07
(000010)E	(1)A <sub>2</sub>	1484.06	1484.25	0.19	1484.17	0.11	-0.07
(100000)A <sub>1</sub>	(0)A <sub>2</sub>	2207.72	2207.73	0.01	2207.53	-0.19	-0.19
(100000)A <sub>1</sub>	(1)E	2209.12	2209.13 ± 0.00	0.01	2208.94	-0.18	-0.19
(000002)E	(1)E	2319.86	2320.67 ± 0.09	0.81	2319.33	-0.53	-1.34
(000002)A <sub>1</sub>	(0)A <sub>2</sub>	2323.88	2325.35	1.47	2323.70	-0.18	-1.65
(000002)A <sub>1</sub>	(1)E	2324.89	2329.16 ± 0.05	4.27	2325.18	0.29	-3.98
(000002)E	(0)E	2330.87	2333.63 ± 3.56	2.76	2330.33	-0.54	-3.30
(000002)E	(1)A <sub>2</sub>	2344.87	2347.27	2.40	2344.31	-0.56	-2.96
(000002)E	(1)A <sub>1</sub>	2344.87	2347.30	2.43	2344.31	-0.56	-2.99
(001001)E	(1)A <sub>2</sub>	2468.15	2468.96	0.81	2467.58	-0.57	-1.38
(001001)E	(1)A <sub>1</sub>	2468.29	2469.10	0.81	2467.72	-0.57	-1.38
(001001)E	(0)E	2472.93	2473.92 ± 2.23	0.99	2472.36	-0.57	-1.56
(001001)E	(1)E	2480.76	2481.94 ± 0.00	1.18	2480.18	-0.58	-1.76
(002000)A <sub>1</sub>	(0)A <sub>2</sub>	2605.11	2606.64	1.53	2604.55	-0.56	-2.09
(002000)A <sub>1</sub>	(1)E	2606.65	2608.18 ± 0.01	1.53	2606.08	-0.57	-2.09
(000011)E	(1)E	2629.06	2629.70 ± 0.01	0.64	2628.86	-0.20	-0.84
(000011)E	(0)E	2631.27	2631.91 ± 0.67	0.64	2631.06	-0.21	-0.84
(000011)A <sub>1</sub>	(1)E	2634.30	2634.65 ± 0.01	0.35	2634.11	-0.19	-0.53
(000011)E	(1)A <sub>2</sub>	2636.12	2637.74	1.62	2635.90	-0.22	-1.85
(000011)E	(1)A <sub>1</sub>	2636.12	2637.75	1.63	2635.90	-0.22	-1.85
(000011)A <sub>1</sub>	(0)A <sub>2</sub>	2640.99	2642.75	1.76	2640.81	-0.18	-1.94
(000011)A <sub>2</sub>	(0)A <sub>1</sub>	2642.69	2643.34	0.65	2642.49	-0.20	-0.85
(000011)A <sub>2</sub>	(1)E	2652.04	2653.09 ± 0.03	1.05	2651.85	-0.19	-1.23
(001010)E	(1)E	2781.91	2782.69 ± 0.00	0.78	2782.27	0.36	-0.42
(001010)E	(0)E	2783.96	2784.19 ± 0.58	0.23	2783.73	-0.23	-0.46
(001010)E	(1)A <sub>1</sub>	2788.17	2788.41	0.24	2787.94	-0.23	-0.47
(001010)E	(1)A <sub>2</sub>	2788.25	2788.50	0.25	2788.02	-0.23	-0.48

TABLE VI. Experimental and calculated rotational energy levels of  $\text{CHD}_3$  (in  $\text{cm}^{-1}$ ). The columns are as in Table II. The experimental values are from Ref. 62

State	Exp.	SSDP	SSDP-Exp.	NEKCB	NEKCB-Exp.	NEKCB-SSDP
(1,1)E	5.908	$5.906 \pm 0.000$	-0.002	5.907	-0.001	0.001
(1,0)A <sub>2</sub>	6.558	6.556	-0.002	6.557	-0.001	0.001
(3,3)A <sub>-</sub>	33.494	33.483	-0.011	33.486	-0.008	0.003
(3,3)A <sub>+</sub>	33.494	33.483	-0.011	33.486	-0.008	0.003
(3,2)E	36.744	$36.731 \pm 0.001$	-0.013	33.736	-0.008	0.005
(3,1)E	38.693	$38.678 \pm 0.001$	-0.015	38.685	-0.008	0.007
(3,0)A <sub>2</sub>	39.343	39.327	-0.016	39.335	-0.008	0.008
(5,5)E	82.096	$82.067 \pm 0.000$	-0.029	82.076	-0.020	0.009
(5,4)E	87.943	$87.906 \pm 0.000$	-0.037	87.922	-0.020	0.016
(5,3)A <sub>-</sub>	92.488	92.443	-0.045	92.468	-0.021	0.025
(5,3)A <sub>+</sub>	92.488	92.444	-0.044	92.468	-0.021	0.024
(5,2)E	95.735	$95.682 \pm 0.007$	-0.053	95.714	-0.021	0.032
(5,1)E	97.682	$97.624 \pm 0.008$	-0.058	97.661	-0.021	0.037
(5,0)A <sub>2</sub>	98.331	98.271	-0.060	98.310	-0.021	0.039
(10,10)E	295.378	$295.274 \pm 0.000$	-0.104	295.306	-0.072	0.032
(10,9)A <sub>1/2</sub>	307.698	$307.644 \pm 0.000$	-0.054	307.625	-0.073	-0.019
(10,8)E	318.714	$318.735 \pm 0.000$	0.021	318.640	-0.074	-0.095
(10,7)E	328.427	$328.517 \pm 0.000$	0.090	328.352	-0.075	-0.165
(10,6)A <sub>1/2</sub>	336.840	$336.976 \pm 0.001$	0.136	336.765	-0.075	-0.212
(10,5)E	343.955	$344.105 \pm 0.005$	0.150	343.879	-0.075	-0.226
(10,4)E	349.774	$349.909 \pm 0.008$	0.135	349.698	-0.076	-0.211
(10,3)A <sub>-</sub>	354.299	354.362	0.063	354.222	-0.077	-0.140
(10,3)A <sub>+</sub>	354.299	354.417	0.118	354.222	-0.077	-0.195
(10,2)E	357.530	$357.510 \pm 0.033$	-0.020	357.453	-0.077	-0.057
(10,1)E	359.468	$359.718 \pm 1.190$	0.249	359.391	-0.077	-0.327
(10,0)A <sub>1</sub>	360.114	360.713	0.599	360.037	-0.077	-0.676

TABLE VII. Some  $J = 1$  experimental and calculated rotational energy levels of  $\text{CHD}_3$  (in  $\text{cm}^{-1}$ ). First column: number of quanta in the vibrational modes and symmetry of the vibrational state, second column: symmetry of the rotational state with value of  $K$ , third column: experimental values taken from Ref.<sup>60,63–65</sup>, fourth column: results with the SSDP method using the WC PES, fifth column: the difference between SSDP energies and experimental values, sixth column: results with the NEKCB method and the same PES, seventh column: the difference between the NEKCB energies and the experimental values, eighth column: the difference between the NECCB and SSDP energies.

Vib	(K)Sym	Exp.	SSDP	SSDP-Exp.	NEKCB	NEKCB-Exp.	NEKCB-SSDP
(000000)A <sub>1</sub>	(1)E	5.91	5.91 ± 0.00	0.00	5.91	0.00	0.00
(000000)A <sub>1</sub>	(0)A <sub>2</sub>	6.55	6.56	0.01	6.56	0.01	0.00
(001000)A <sub>1</sub>	(1)E	1010.04	1009.50 ± 0.01	-0.54	1009.49	-0.55	-0.01
(001000)A <sub>1</sub>	(0)A <sub>2</sub>	1010.24	1009.70	-0.54	1009.70	-0.54	0.00
(000001)E	(1)E	1040.68	1040.29 ± 0.00	-0.40	1040.26	-0.43	-0.03
(000001)E	(0)E	1042.90	1042.49 ± 0.06	-0.41	1042.47	-0.43	-0.02
(000001)E	(1)A <sub>2</sub>	1043.76	1042.58	-1.18	1042.49	-1.27	-0.09
(000001)E	(1)A <sub>1</sub>	1043.92	1043.37	-0.55	1043.33	-0.59	-0.04
(000010)E	(1)A <sub>2</sub>	1294.85	1294.83	-0.02	1294.77	-0.08	-0.06
(000010)E	(1)A <sub>1</sub>	1294.89	1294.88	-0.01	1294.81	-0.08	-0.07
(000010)E	(0)E	1299.07	1299.05 ± 0.07	-0.02	1298.98	-0.09	-0.07
(000010)E	(1)E	1302.00	1301.98 ± 0.01	-0.03	1301.91	-0.09	-0.07
(002000)E	(1)E	1996.66	1998.46 ± 0.01	1.79	1995.84	-0.83	-2.62
(002000)E	(0)A <sub>2</sub>	1996.91	1998.73	1.78	1996.11	-0.84	-2.62
(001001)E	(1)E	2045.23	2044.49 ± 0.02	-0.74	2044.46	-0.77	-0.03
(001001)E	(0)E	2046.09	2045.44 ± 0.52	-0.65	2045.33	-0.76	-0.11
(001001)E	(1)A <sub>2</sub>	2046.62	2046.08	-0.54	2045.87	-0.75	-0.21
(001001)E	(1)A <sub>1</sub>	2048.43	2047.80	-0.63	2047.65	-0.78	-0.15
(000002)A <sub>1</sub>	(1)E	2065.91	2065.47 ± 0.10	-0.44	2065.19	-0.72	-0.28
(000002)A <sub>1</sub>	(0)A <sub>2</sub>	2073.96	2067.51	-6.45	2067.19	-6.77	-0.32
(000002)E	(1)A <sub>1</sub>	2067.92	2069.49	1.58	2069.41	1.49	-0.08
(000002)E	(1)A <sub>2</sub>		2069.51		2069.46		-0.05
(000002)E	(0)E		2073.26 ± 0.26		2073.16		-0.10
(000002)E	(1)E	2075.38	2074.75 ± 0.10	-0.64	2074.64	-0.75	-0.11
(010000)A <sub>1</sub>	(1)E	2148.45	2148.66 ± 0.00	0.21	2148.65	0.20	-0.01
(010000)A <sub>1</sub>	(0)A <sub>2</sub>	2149.10	2149.32	0.22	2149.30	0.20	-0.02
(000100)E	(1)A <sub>2</sub>	2255.34	2255.09	-0.26	2255.16	-0.18	0.07
(000100)E	(1)A <sub>1</sub>	2255.35	2255.10	-0.24	2255.16	-0.19	0.06
(000100)E	(0)E	2257.28	2257.04 ± 0.08	-0.24	2257.10	-0.17	0.06
(000100)E	(1)E	2257.97	2257.74 ± 0.01	-0.25	2257.81	-0.17	0.07
(001010)E	(1)A <sub>1</sub>	2303.45	2303.28	-0.28	2303.14	-0.31	-0.14
(001010)E	(1)A <sub>2</sub>	2303.57	2303.37	-0.08	2303.23	-0.33	-0.14
(001010)E	(0)E	2306.89	2306.61 ± 0.27	-0.28	2306.47	-0.42	-0.14
(001010)E	(1)E	2309.78	2309.49 ± 0.01	-0.29	2309.34	-0.44	-0.15

TABLE VIII. Some experimental and calculated rotational energy levels of CH<sub>3</sub>F (in cm<sup>-1</sup>). First column: the labels of the eigenstates with the format “(J,K) symmetry”, second column: experimental values<sup>67,68</sup>, third column: SSDP energies using the PES of Ref. 27, fourth column: the difference between SSDP energies and the experimental values, fifth column: the relative SSDP error, sixth column: the relative difference between the energies of Ref. 69 and the Experimental values.

State	Exp.	SSDP	SSDP-Exp.	Error (%)	Ref. 69 -Exp.
(1,0)A <sub>2</sub>	1.704	1.700	-0.004	-0.210	-0.4 × 10 <sup>-4</sup>
(1,1)E	6.034	6.018 ± 0.000	-0.016	-0.260	0.3 × 10 <sup>-4</sup>
(3,0)A <sub>2</sub>	10.221	10.197	-0.024	-0.237	-2.4 × 10 <sup>-4</sup>
(3,1)E	14.551	14.515 ± 0.001	-0.036	-0.249	-1.7 × 10 <sup>-4</sup>
(3,2)E	27.540	27.468 ± 0.000	-0.072	-0.262	0.3 × 10 <sup>-4</sup>
(3,3)A <sub>1</sub>	49.186	49.053	-0.133	-0.270	3.6 × 10 <sup>-4</sup>
(3,3)A <sub>2</sub>	49.186	49.053	-0.133	-0.270	3.6 × 10 <sup>-4</sup>
(5,0)A <sub>2</sub>	25.553	25.492	-0.061	-0.237	-6.0 × 10 <sup>-4</sup>
(5,1)E	29.882	29.810 ± 0.004	-0.073	-0.243	-5.3 × 10 <sup>-4</sup>
(5,2)E	42.870	42.762 ± 0.000	-0.108	-0.253	-3.4 × 10 <sup>-4</sup>
(5,3)A <sub>1</sub>	64.514	64.346	-0.168	-0.261	-0.2 × 10 <sup>-4</sup>
(5,3)A <sub>2</sub>	64.514	64.346	-0.168	-0.261	-0.2 × 10 <sup>-4</sup>
(5,4)E	94.810	94.558 ± 0.000	-0.252	-0.266	4.3 × 10 <sup>-4</sup>
(5,5)E	133.751	133.394 ± 0.000	-0.357	-0.267	9.9 × 10 <sup>-4</sup>

TABLE IX. Basis sets parameters for NEKCB calculations of levels of CH<sub>3</sub>D.

Bend basis	$l_x = m_x$	$N_\theta$	$N_\phi$	$V_b^{\text{ceil}} (\text{cm}^{-1})$	$N_{\text{FBR}} (\times 10^6)$	$N_{\text{DVR}} (\times 10^3)$	$\rightarrow$	$E_b^{\text{cut}} (\text{cm}^{-1})$	$N_b$
Basis b2	29	30	60	20000.	6.67	678	$\rightarrow$	10490.	962
Stretch basis	$N_r(\text{CH})$	$N_r(\text{CD})$	$V_s^{\text{cut}} (\text{cm}^{-1})$		$N_{\text{DVR}}$		$\rightarrow$	$E_s^{\text{cut}} (\text{cm}^{-1})$	$N_s$
Basis s1	10	14	30000.		6966		$\rightarrow$	20000.	348
Vibrational basis	Bend basis		Stretch basis		$N_{\text{PC}}$	$\rightarrow$		$E_v^{\text{cut}} (\text{cm}^{-1})$	$N_{\text{vib}}$
Basis b2s1v1	b2		s1		$962 \times 348$	$\rightarrow$		8000.	878
Basis b2s1v2	b2		s1		$962 \times 348$	$\rightarrow$		9000.	1589

 TABLE X. Basis sets parameters for NEKCB calculations of levels of CHD<sub>3</sub>.

Bend basis	$l_x = m_x$	$N_\theta$	$N_\phi$	$V_b^{\text{ceil}} (\text{cm}^{-1})$	$N_{\text{FBR}} (\times 10^6)$	$N_{\text{DVR}} (\times 10^3)$	$\rightarrow$	$E_b^{\text{cut}} (\text{cm}^{-1})$	$N_b$
Basis b0	35	36	72	20000.	16.6	1255	$\rightarrow$	9200.	989
Stretch basis	$N_r(\text{CH})$	$N_r(\text{CD})$	$V_s^{\text{cut}} (\text{cm}^{-1})$		$N_{\text{DVR}}$		$\rightarrow$	$E_s^{\text{cut}} (\text{cm}^{-1})$	$N_s$
Basis s1	10	10	30000.		7021		$\rightarrow$	20000.	562
Vibrational basis	Bend basis		Stretch basis		$N_{\text{PC}}$	$\rightarrow$		$E_v^{\text{cut}} (\text{cm}^{-1})$	$N_{\text{vib}}$
Basis b0s1v1	b0		s1		$989 \times 562$	$\rightarrow$		8000.	1833
Basis b0s1v2 (not done)	b0		s1		$989 \times 562$	$\rightarrow$		8500.	2515