Using nondirect product Wigner D basis functions and the Symmetry Adapted Lanczos algorithm to compute the ro-vibrational spectrum of $\text{CH}_4\text{-H}_2\text{O}$

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Abstract

By doing calculations on the methane-water Van der Waals complex, we demonstrate that highly converged energy levels and wavefunctions can be obtained using Wigner D basis functions and the Symmetry Adapted Lanczos (SAL) method. The Wigner D basis is a nondirect product basis and therefore efficient when the kinetic energy operator has accessible singularities. The SAL makes it possible to exploit symmetry to label energy levels and reduce the cost of the calculation, without explicitly using symmetry-adapted basis functions. Line strengths are computed and new bands are identified.

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I. INTRODUCTION

In this paper, we demonstrate the advantages of using Wigner D basis functions and the symmetry adapted Lanczos eigensolver for computing the ro-vibrational spectrum of a Van der Waals (VdW) dimer. The particular dimer we study is the methane-water (MW) complex. MW has been the focus of previous experimental[1, 2] and theoretical[3–7] papers. Van der Waals complexes in which one of the monomers is H_2O are studied in part because interactions between water and other molecules play an important role in many biochemical and chemical processes. Spectroscopy provides a means of evaluating and possibly refining inter-molecular potential energy surfaces. [8, 9]

For decades, it has been possible to measure highly resolved ro-vibrational spectra of VdW dimers. It is also now possible for experts to make extremely accurate inter-molecular (the monomers are rigid) potential energy surfaces (PESs). [10–12] From a PES one can immediately identify the most stable structure of a dimer and compute harmonic frequencies in the most stable well. However, VdW dimers frequently have several low-lying minima and their vibrations are notoriously anharmonic and coupled. Because some of the vibrations have small frequencies, coupling between vibration and rotation is, in general, also important. To analyse and assign an experimental spectrum, one therefore needs in addition to a PES a computational procedure for solving the ro-vibrational Schrödinger equation.

Several computational methods are used to solve the ro-vibrational Schrödinger equation for dimers. The calculations are difficult because there are 6 strongly coupled inter-molecular vibrational coordinates. In addition, three Euler angles are required to fully describe the orientation of the dimer. GENIUSH[13, 14] is one powerful method for computing spectra of polyatomic molecules, including VdW dimers. When using GENIUSH, one is free to choose the best possible vibrational coordinates. This is possible because coefficients of derivatives in the kinetic energy operator (KEO) are computed numerically. In GENIUSH, matrix elements of the KEO, in a direct product discrete variable representation (DVR) [15–17] are obtained by evaluating the coefficients at points. There is no need to know the KEO as an equation. This makes GENIUSH widely applicable. It is a very useful black-box procedure. Another useful strategy is to divide coordinates into two groups, solve separate problems for both groups with an iterative eigensolver, and then combine the separate solutions to

solve the full problem. [18–21]. By using intra-molecular and inter-molecular groups and exploiting the fact that not many intra solutions are required, Felker and Bacic have done calculations for $\text{H}_2\text{O}-\text{CO}$, $\text{HDO}-\text{CO}$ and benzene- H_2O in which the H_2O monomer is flexible. [22–24]. By solving a separate problem for only the intra coordinates, it is possible to do 12-D calculations for water dimer. [25]. In this paper we solve only the inter problem.

In principle, it is always advantageous to look for vibrational coordinates that minimize the importance of coupling. In practice, when coupling between the two monomers of a VdW dimers is weak, Euler angles that specify the orientation of monomer fixed (MF) frames attached to the two monomers with respect to a dimer fixed (DF) frame attached to the vector between the centres of mass of the two monomers are excellent vibrational coordinates. Even when there is significant coupling between the monomers, it is hard to find better coordinates. In practice therefore, the full generality of GENIUSH is not required for VdW dimers. The KEO in terms of MF Euler angles, the length of the inter-monomer vector, and the angles that specify the orientation of that vector was derived by Brocks et al.[26]. These coordinates will be referred to collectively as Euler coordinates.

If one uses Euler coordinates, it is natural to write the KEO in terms of angular momentum operators and to use Wigner D basis functions. [27] They are eigenfunctions of part of the KEO. Matrix elements of all terms in the KEO are easily computed from equations derived by applying angular momentum operators to the basis functions. A more important advantage of using Wigner D basis functions is that they easily deal with singularities in the KEO. For molecules with more than three atoms, all KEOs have singularities. They occur at points at which a vibrational coordinate becomes undefined. If $\alpha_A, \beta_A, \gamma_A$ and $\alpha_B, \beta_B, \gamma_B$ are the Euler angles of the monomers A and B, and α, β are the angles that specify the orientation of the inter-monomer vector then the KEO is singular when β_A, β_B , or β is 0 or π . Wigner D basis functions are nondirect product functions. They have shared indices. There is a direct link between the existence of singularities in the KEO and the nondirect product character of the basis. In most cases, it is possible to use, instead of the Wigner D basis, a larger direct product basis (as is done for example in GENIUSH). However, when using an iterative eigensolver, it is particularly advantageous to use a nondirect product basis because it reduces the spectral range of the Hamiltonian matrix and hence the number of required iterations. [28] Another advantage of the Wigner D basis functions is that

they do not depend on adjustable parameters (e.g. coordinate ranges). One needs only to choose maximum values of the indices. Wigner D basis functions have non-zero amplitude everywhere in configuration space. They have been used to solve many 6-D inter-molecular dimer systems such as water dimer[25, 29–34], ammonia dimer[35], benzene dimer [36].

A disadvantage of Wigner D basis functions is the need to use quadrature (unless the PES is represented as a basis function expansion [9]). It is not possible to make a DVR basis that spans the same space as a nondirect product VBR[16] (variational basis representation) basis, has the same number of functions, and in which the overlap matrix is an identity matrix. [37] However, this is not a serious failing because it is straightforward to evaluate potential integrals by quadrature. It is necessary to use more points than VBR basis functions and to evaluate sums sequentially. This machinery is well established. [16, 28, 30, 38–42]

A major theme of this paper is the advantage of using SAL to exploit symmetry. [41, 43, 44] It is of course widely appreciated that symmetry makes it possible to reduce the cost of computing a spectrum and that symmetry labels are important for understanding spectra. When a direct eigensolver is used to diagonalize a matrix, one makes symmetry adapted basis functions and thereby block diagonalizes the matrix and reduces the cost of diagonalization. The size of the matrix increases rapidly with dimension and if there are enough coordinates, the blocks are so large that a direct eigensolver cannot be used. Iterative methods are therefore methods of choice. Using symmetry adapted basis functions complicates the evaluation of the matrix-vector products required to use an iterative eigensolver. Instead, it is better to use simple basis functions and SAL to calculate states labelled by the irreducible representations (irreps). This is done with projection operators. Using SAL is straightforward if all group operations affect basis functions in a simple way. For $\text{CH}_4\text{-H}_2\text{O}$, we therefore use projection operators for a subgroup of the full molecular symmetry group. We can nonetheless label wavefunctions with irreps of the full group by using the correlation table between the subgroup and the full group. [45–47]

The Wigner D basis has amplitude everywhere in the rigid-monomer configuration space. Therefore, wavefunctions computed with the Wigner D basis are eigenfunctions of E^* , despite the fact that E^* is not a feasible operation for the non-rigid monomer calculation. For this reason, we use a parity adapted (PA) basis and apply SAL within each parity block. Because we work in the inter-monomer subspace we find some peculiar results. For example, we find

that all E_a states have even parity and all E_b states have odd parity.

Ro-vibrational levels of $\text{CH}_4\text{-H}_2\text{O}$ were calculated[5, 6] with GENIUSH on the AOSz05 PES of Ref. 3, on the QCHB15 PES of Ref. 4, and on the more recent WM19 PESRef. 7. No symmetry was utilised in the GENIUSH calculations and irrep labels were assigned by doing a reduced-dimensional calculation after the full GENIUSH calculation.[6]. Due to the use of a direct product DVR basis, the GENIUSH calculation is less accurate than the calculation with Wigner D basis and requires a large basis. Since one goal of our study is to compare GENIUSH with the use of SAL, Euler coordinates, and the Wigner D basis, for a VdW dimer, we choose to use the AOSz05 PES[3]. It is more accurate and rotational levels to many digits are only reported on the AOSz05 PES of Ref. 5. We do not assign irrep labels *after* energy levels are computed, but exploit symmetry *during* the calculation of the levels. Our irrep labels are certain. The advantage of the Wigner D basis makes it possible for us to converge levels very accurately. We have computed energy level differences between members of doublets in the spectrum. The doublet splitting is as small as $\sim 10^{-5} \text{ cm}^{-1}$. We compute intensities and identify many new bands. We also identify a K misassignment by Dore et al.[1]

II. KINETIC ENERGY OPERATOR

We force both monomers to be rigid and use the KEO of Brocks et al. [26] The coordinates are:

$$\begin{aligned} \text{rotation} &: \alpha, \beta \\ \text{vibration} &: (r_0, \alpha_A, \beta_A, \gamma_A, \alpha_B, \beta_B, \gamma_B) . \end{aligned} \quad (1)$$

(α, β) are Euler angles that specify the orientation of a dimer-fixed (DF) frame whose z axis is along the inter-monomer Jacobi vector and points from water to methane. The length of the inter-monomer vector is r_0 . $(\alpha_A, \beta_A, \gamma_A)$ and $(\alpha_B, \beta_B, \gamma_B)$ specify the orientation of monomer-fixed (MF) frames attached to the monomers with respect to the DF frame. Monomer A is H_2O and monomer B is CH_4 . The PES depends on only six of the vibrational coordinates because one can think of α_A as a third rotational coordinate.

The KEO of Brocks *et al.*[26] is

$$T = T^A(\mathbf{j}_A) + T^B(\mathbf{j}_B) + T_{int}(\mathbf{Q}; \mathbf{p}_{r_0}, \mathbf{j}_A, \mathbf{j}_B, \mathbf{J}) , \quad (2)$$

where $\mathbf{Q}$ denotes all the vibrational coordinates. According to Brocks *et al.*, these terms are,

$$T^X = \frac{1}{2} \mathbf{j}_X^\dagger \mathbf{\Gamma}_X \mathbf{j}_X, \quad X = A, B; \quad (3)$$

$$T_{int} = -\frac{1}{2\mu_0} \frac{\partial^2}{\partial r_0^2} + B_0(r_0) \left[\mathbf{J}^2 - \cot \beta \frac{\partial}{\partial \beta} + (\mathbf{j}_A + \mathbf{j}_B)^2 - 2(\mathbf{j}_A + \mathbf{j}_B) \cdot \mathbf{J} \right] . \quad (4)$$

T^X is a rigid rotor KEO for monomer X. $\mathbf{\Gamma}_X$, $X = A, B$, is diagonal. Its diagonal elements are rigid rotor rotational constants. T_{int} includes all the inter-monomer terms and it depends on the coordinates $\mathbf{Q}$. $B_0(r_0) = 1/(2\mu_{r_0} r_0^2)$. μ_{r_0} is the reduced mass of the dimer. $\mathbf{J}$ is the total angular momentum. Components of *all* the angular momentum operators in T_{int} are in the DF frame. In contrast, the components of angular momentum operators in T^A and T^B are in the MF frames. $\mathbf{j}_X$ in T_{int} and in T^X are therefore projected onto different frames, their commutation relations are different and different analytic expressions must be used, see Refs. 9, 25, 26, 48, 49. To simplify the notation, we do not label $\mathbf{j}_X$ in T^X with MF.

III. MOLECULAR SYMMETRY (MS) GROUP CONSTRUCTED AS $G_{48} = T_d(M) \otimes S_2$

The permutation inversion (PI) group [50] for the dimer, excluding permutation operations that permute H atoms in different monomers, is the G_{96} PI group. It is naturally obtained from the direct product of three groups: the permutation group S_4 of CH_4 (permuting the 4 H), the permutation group S_2 of H_2O (permuting its 2 H), and the inversion group $\{E, E^*\}$. We label the H atoms of methane with 1, 2, 3, 4, and the H atoms of water with a and b and write, $G_{96} = S_4 \otimes S_2 \otimes \{E, E^*\}$ where $S_2 = \{E, (ab)\}$. G_{96} contains (48) infeasible operations such as E^* and the permutation (23). Operations that are infeasible for CH_4 are also infeasible for the dimer. To obtain the molecular symmetry (MS) group [50], which by definition is composed of all the feasible PI operations, one must remove the infeasible operations. To define labels for the characters, we think of the MS group as $G_{48} = T_d(M) \otimes S_2$, where $T_d(M)$ is the feasible PI group of CH_4 (isomorphic to the point group T_d) derived by removing infeasible operations from the full PI group of CH_4 . We follow Bunker and Jensen

and add “(M)” to the point group T_d [50]. Using the product structure $T_d(M) \otimes S_2$, it is simple to build the character table of G_{48} from the character tables of $T_d(M)$ (taken from Table A-14 of Ref. 50) and S_2 . This is the same approach taken by Bunker and Jensen to build the character table of $\tilde{G}_{48}$ of CH_4 (Table A-29 of Ref. 50) by using $\tilde{G}_{48} = T_d(M) \otimes \{E, E^*\}$. Our G_{48} character table is the same as Table A-29 of Ref. 50, but because we replace E^* with (ab) , in our case $+/-$ means symmetric/anti-symmetric for the (ab) operation, rather than even and odd parity. The irrep labels we use for G_{48} are therefore a combination of symmetry labels of $T_d(M)$ and S_2 . Our labels have the advantage that, for example, for an A_1^- dimer state, the characters of the operations in G_{48} that are also in $T_d(M)$ are exactly the same as those of a methane A_1 state. For completeness, our G_{48} character table is given in Table VI.

Although systematic and logical, our choice of the irrep labels has the disadvantage that it is not consistent with Ref. 1 and Ref. 5. Dore *et al.*[1] mistakenly included all CH_4 permutations in their group and constructed G_{48} from $G_{48} = S_4 \otimes \{E, (ab)\}$. This is wrong because they included infeasible operations and omitted feasible operations that involve E^* . Sarka *et al.*[5] recognized that Dore *et al.*'s group included infeasible operations and replaced Dore *et al.*'s $(1423)(ab)$, $(23)(ab)$, (1423) and (23) with $(1423)^*(ab)$, $(23)^*(ab)$, $(1423)^*$ and $(23)^*$ to make all operations in the group feasible. We and Sarka *et al.* have the same group but different names for the irreps. The only difference is that **for “−” states (anti-symmetric H_2O states), the 1 and 2 subscripts of the Sarka *et al.* symmetry labels must be interchanged to obtain our symmetry labels**. Hence, their A_1^- , A_2^- , F_1^- and F_2^- are our A_2^- , A_1^- , F_2^- and F_1^- , respectively.

In this paper, the two monomers are rigid and the PES has 24 wells. The complete PES has two sets of 24 wells and the two sets are separated by high barriers. If the monomers are flexible then E^* is infeasible, however, if the monomers are rigid then one can still define E^* and give states parity labels. States can be labelled with irreps of $G_{48} \otimes \{E, E^*\}$. It is a semi-direct product because E^* does not commute with G_{48} operations when the monomers are rigid. Although it is a semi-direct product, we can label the states we compute by an irrep of G_{48} and a parity label. However, some parity properties of states computed with rigid monomers are not the same as those of states computed with flexible monomers. This is due to the fact that E^* affects both the intra-molecular (CH_4 only) and inter-molecular

coordinates, but that in a rigid-monomer calculation one allows E^* to affect only the inter-molecular coordinates.

IV. BASIS FUNCTIONS AND PARITY ADAPTATION

In the variational calculation, each basis function is a product of a discrete variable representation function for r_0 and a ro-vibrational basis function written in terms of the 8 angles. The simplest ro-vibrational basis functions are the primitive uncoupled functions,

$$|\xi\rangle = |j_A k_A m_A; j_B k_B m_B; J K M\rangle, \quad (5)$$

where

$$\begin{aligned} \langle \alpha_A, \beta_A, \gamma_A | j_A k_A m_A \rangle &= \sqrt{\frac{2j_A + 1}{8\pi^2}} D_{m_A k_A}^{j_A}(\alpha_A, \beta_A, \gamma_A)^* \\ \langle \alpha_B, \beta_B, \gamma_B | j_B k_B m_B \rangle &= \sqrt{\frac{2j_B + 1}{8\pi^2}} D_{m_B k_B}^{j_B}(\alpha_B, \beta_B, \gamma_B)^* \\ \langle \alpha, \beta, 0 | J K M \rangle &= \sqrt{\frac{2J + 1}{4\pi}} D_{MK}^J(\alpha, \beta, 0)^*, \end{aligned} \quad (6)$$

with D_{MK}^J being a Wigner function. [27] The constraint $K \equiv m_A + m_B$ is imposed on the basis indices. Although these primitive basis functions are labelled by m_A , it is not an independent quantum number. It is because of the $K \equiv m_A + m_B$ constraint that matrix elements of the KEO are simple and none of the integrals are singular.

Knowing that wavefunctions of the rigid-monomer Hamiltonian computed in the basis of Eq. (5) must be eigenfunctions of E^* , we prefer to work with a parity-adapted (PA) basis that has the advantage of being two times smaller. Each parity adapted basis function is a linear combination of two (or a single) $|\xi\rangle$ functions. To define PA basis functions, one needs to know how E^* affects $|\xi\rangle$, which of course depends on how E^* affects the coordinates. Even when studying an isolated molecule (monomer), the effect of E^* on the Euler angles that specify the orientation of the molecule fixed frame (with respect to a space fixed frame) depends on the definition of the frame. When studying a dimer, the MF frames are defined with respect to the DF frame and the effect of E^* on the MF Euler angles is not the same as for an isolated molecule. The effect is different for different choices of the MF axes. There are three choices, which we call Cases in the Appendix B of Ref. 49. In this paper, we use

Case II and attach the MF z axis to one vector and the y axis to the cross product of that vector and another vector (see section V). Because we use Case II,

$$u_{j_A k_A m_A; j_B k_B m_B; K}^{JMP} = N_{k_A k_B m_A K} \frac{1}{\sqrt{2}} \\ [|j_A k_A m_A; j_B k_B m_B; JKM\rangle + (-1)^{J+k_A+k_B+P} |j_A \bar{k}_A \bar{m}_A; j_B \bar{k}_B \bar{m}_B; J\bar{K}\bar{M}\rangle] , \quad (7)$$

with

$$N_{k_A k_B m_A K} = (1 + \delta_{k_A,0} \delta_{k_B,0} \delta_{m_A,0} \delta_{K,0})^{-1/2} ,$$

where $P = 0$ and 1 correspond to even and odd parity, respectively. The ranges of labels for the parity-adapted basis functions are restricted, as given in Eq. A10 of Ref. 25. After setting $M = 0$, the parity-adapted basis functions are real for $(-1)^{J+P} = 1$ and pure imaginary for $(-1)^{J+P} = -1$. We do different calculations for even and odd states.

V. USE OF SUBGROUP $C_{3v}(\text{M}) \otimes S_2$

Within each parity block, it is in principle possible to exploit the symmetry of $G_{48} = T_d(\text{M}) \otimes S_2$. Because some of the operations in G_{48} affect our coordinates in a complicated way, we instead exploit the symmetry of $C_{3v}(\text{M}) \otimes S_2$. We obtain energies (and wavefunctions) and irrep assignments, from the same calculation, by using the PA basis (Eq. (7)), $C_{3v}(\text{M}) \otimes S_2$ projection operators, and the symmetry adapted Lanczos (SAL) method. [41, 43, 44] All matrix-vector products are evaluated by doing sums sequentially. [16, 30, 41, 51, 52] The only short-coming of this strategy is that one must use a correlation table to recover the full group labels from the subgroup labels. To do this, it is necessary to identify states with different subgroup irreps which should be degenerate and must transform like a single multi-dimensional irrep of the full group. These nearly-degenerate levels only become degenerate if the basis set is sufficiently large. The same idea was used with the subgroup $C_{3v}(\text{M})$ to compute ro-vibrational levels of CH_4 whose full group is $T_d(\text{M})$. [47]

Other strategies for assigning irrep labels are possible. Sarka *et al.* assigned irrep labels to the dimer energies they computed with their GENIUSH program by doing a second GENIUSH calculation. From the second (5-D) calculation, done for a dimer with a large and fixed value of r_0 and $V=0$, they obtained what they called coupled rotor (CR) states. They analysed the CR states to assign to them G_{48} irrep labels. Having done this they

were able to assign G_{48} irreps to the 6-D GENIUSH dimer wavefunctions, by calculating overlaps of them with the CR states. It would also be possible to use basis functions that transform like irreps of G_{48} . Van der Avoird and co-workers use such a basis in their work on $\text{CH}_4\text{-Ar}$.^[48] Their symmetry-adapted basis functions are complicated linear combinations of $|j_B k_B m_B\rangle$ (for CH_4), and they depend on j_B . Moreover, orthogonalizations are required when the basis, for a given j_B contains a particular irrep more than once. One can easily use this symmetry-adapted basis if one stores the Hamiltonian matrix. It is, however, difficult to use it efficiently with an iterative eigensolver. Because we use SAL, we prefer to work with a group for which the projection operators are simpler.

To use SAL, we need projection operators. In previous papers, we defined $C_{3v}(\text{M})$ projection operators in terms of three operators: $(23)^*$, $(12)^*$ and $(13)^*$.^[47, 53] They were derived from C_{3v} representation matrices^[47, 50] and then factorised using the multiplication rule of permutation inversion operators^[50]. Note that the projection operators in Ref. 47 have typos,^[54] but the projection operators in Ref. 53 are correct. In this paper, we re-express the $C_{3v}(\text{M})$ projection operators of Ref. 53 in terms of three operators, $(23)^*$, (123) and (132) and we also put the $(E \pm (23)^*)$ factor on the right (the two factors of the projection operators commute) since we prefer to apply this factor first, for reasons we shall discuss later in this section. The $C_{3v}(\text{M})$ projection operators in this new form are given in Table IV. From the $C_{3v}(\text{M})$ projection operators we make $C_{3v}(\text{M}) \otimes S_2$ projection operators. To use the $C_{3v}(\text{M}) \otimes S_2$ projection operators in each of the parity blocks, we must know the effect of operations in $C_{3v}(\text{M}) \otimes S_2$ on the PA basis functions. This we obtain from their effect on the primitive basis functions which in turn is determined by the way those operations affect the coordinates in our variational calculation.

The way $(\alpha_B, \beta_B, \gamma_B)$ change when $C_{3v}(\text{M})$ operations are applied depends on the definition of the CH_4 MF frame. As discussed in Ref. 49, the way the MF Euler angles change when E^* is applied depends on the Case of the MF frame. There are only three cases if the MF frame is required to be right-handed. In principle, one could use any of the three cases. We choose a case II MF frame because in the primitive basis all matrix elements are real and the PA basis functions are all real and one can use a real-to-complex FFT to compute potential matrix-vector products. In case II, under the inversion operation, the MF x -axis and z -axis are flipped and the y -axis is unchanged. As a result, the MF Euler angles react as

specified in Appendix B of Ref. 49. The case II MF frame for CH₄ is a principal axis frame with its z-axis along one of the CH bonds and aligned with a C_3 axis. The un-normalized axis vectors for the MF frame of CH₄ are:

$$\begin{aligned}\hat{g}_x &= \hat{g}_y \times \hat{g}_z \\ \hat{g}_y &= \overrightarrow{\text{CH}_4} \times \overrightarrow{\text{CH}_1} \\ \hat{g}_z &= \overrightarrow{\text{CH}_4}.\end{aligned}\tag{8}$$

The way $(\alpha_A, \beta_A, \gamma_A)$ for H₂O change when $C_2(\text{M})$ operations are applied depends on the definition of the H₂O MF frame. We again choose a Case II MF frame. The z-axis of the MF frame for H₂O is along the C_2 axis with the O atom having a positive z-value. The x-axis is on the plane of H₂O with H_a having a positive x-value. The effect of the operations of $C_{3v}(\text{M}) \otimes S_2$ group on all the angles is given in Table II. It is straightforward to obtain this table because the angles are affected by the symmetry operations in a simple way.

With Table II in hand, it is possible to determine the effect of the group operators on the primitive basis functions. They are given in Table III. Note, however, that to apply an operation to a function $f(x)$, one uses $\hat{O}f(x) = f(\hat{O}^{-1}x)$. See e.g. Ref. 53. This is important for (123) and (132). Table III is used to determine the effect of $C_{3v}(\text{M})$ projection operators on the PA basis functions. As an example, consider P^{E_b} ,

$$\begin{aligned}P^{E_b}u_{j_A k_A m_A; j_B k_B m_B; K}^{JMP} &= (1/6)[2E - (123) - (132)][E - (23)^*]u_{j_A k_A m_A; j_B k_B m_B; K}^{JMP} \\ &= (1/3)[1 - \cos(\frac{2\pi}{3}k_B)][1 - (-1)^P]u_{j_A k_A m_A; j_B k_B m_B; K}^{JMP} \\ &= \begin{cases} u_{j_A k_A m_A; j_B k_B m_B; K}^{JMP} & \text{if } k_B \neq 0(\text{mod } 3) \text{ and } P = 1 \\ 0 & \text{otherwise} \end{cases},\end{aligned}\tag{9}$$

where we have used

$$[(123) + (132)]u_{j_A k_A m_A; j_B k_B m_B; K}^{JMP} = 2\cos(\frac{2\pi}{3}k_B)u_{j_A k_A m_A; j_B k_B m_B; K}^{JMP}.\tag{10}$$

As summarised in Tables IV and V, we find that even PA basis functions with $k_B = 0(\text{mod } 3)$ are of A_1 symmetry, odd PA basis functions with $k_B = 0(\text{mod } 3)$ are of A_2 symmetry, and that even PA basis functions with $k_B \neq 0(\text{mod } 3)$ are of E_a symmetry, and odd PA basis functions with $k_B \neq 0(\text{mod } 3)$ are of E_b symmetry. For the projection operators $P^\pm =$

$(1/2)[E \pm (ab)]$ of S_2 , PA basis functions with k_A even and k_A odd are of + (para H₂O) and – (ortho H₂O) symmetry, respectively. In summary, from the even PA block we simultaneously compute $(A_1^+, A_1^-, E_a^+, E_a^-)$ levels and from the odd PA block we simultaneously compute $(A_2^+, A_2^-, E_b^+, E_b^-)$ levels.

We then use the correlation between the $C_{3v}(\text{M}) \times S_2$ group and the $T_d(\text{M}) \times S_2$ group to obtain $T_d(\text{M}) \times S_2$ group symmetry labels. The correlation table (cf. Table IV of Ref. 47) is given in Table V. A key step in the assignment of $T_d(\text{M}) \times S_2$ labels is identifying computed levels labelled by A and E $C_{3v}(\text{M})$ irreps that should be degenerate and correspond to a F level. Clearly, this is only possible if the basis convergence error is smaller than gaps between exact energy levels. This requires using an excellent basis, because some of the splittings between F_1 and F_2 splittings are very small. The Wigner basis does the job and in our calculation A and E levels that should be degenerate differ by less than $2 \times 10^{-6} \text{ cm}^{-1}$. This is small enough that we are able to identify nearly degenerate A and E levels. The energies of some of the degenerate components of E and F states occur in different parity blocks. E.g., F_2 of T_d correlates with A_1 , E_a , and E_b of C_{3v} and A_1 and E_a are even levels whereas E_b is an odd level.

The entire calculation could also be done without starting with the PA basis by applying the projection operators to the primitive basis functions. The functions obtained by applying the projection operators to the primitive basis functions are exactly the same as those obtained by applying the same projection operators to the PA basis functions, for reasons we explain below.

It may seem surprising that there are no even E_b states, no odd E_a states and that all A_1 states are even and all A_2 states are odd. This happens because (23) does not affect any of the inter-molecular coordinates and therefore affects functions of inter-molecular coordinates exactly the way as E . For this reason, $E - (23)^*$ when applied to an even function yields zero, and $E + (23)^*$ when applied to an odd function yields zero. Therefore the operator $[E \pm (23)^*]$, which is the last factor in the definition of the four $C_{3v}(\text{M})$ projection operators, behaves like $[E \pm E^*]$. The unusual affect of (23) is partly due to omitting the intra-molecular coordinates and partly due to the choice of the frame (Case). In a calculation with only inter-molecular coordinates, the states that are missing from the even and odd blocks will depend on the Case of the MF axes.

Note that in a full calculation, using both intra-molecular and inter-molecular coordinates, there are no permutation operations that leave all the coordinates unchanged. No states would be missing from the even and odd blocks if we did a calculation using all the inter- and intra-molecular coordinates. To do such a calculation, it would be natural to use basis functions that are products of an intra factor Ψ_{intra} and an inter factor Ψ_{inter} . Inter factors are obtained from a rigid-monomer calculation, as in this paper. Some have even parity, Ψ_{inter}^e , and some have odd parity, Ψ_{inter}^o . Each intra factor also has either even or odd parity, assuming the full PES is used (any monomer with more than 3 atoms has wavefunctions with even parity and wavefunctions with odd parity). We denote the intra factors Ψ_{intra}^e and Ψ_{intra}^o . Full-dimensional even states could be obtained from a basis whose functions can be divided into two blocks and has the form (we omit the odd basis because it is similar),

$$\begin{pmatrix} |\Psi_{\text{intra}}^e\rangle |\Psi_{\text{inter}}^e\rangle \\ |\Psi_{\text{intra}}^o\rangle |\Psi_{\text{inter}}^o\rangle \end{pmatrix}. \quad (11)$$

In the simplest full-dimensional calculation, one would keep the two intra states with the lowest energy. They are the even and odd components of the ground state of CH_4 . If we neglect all coupling between inter and intra coordinates then the matrix elements that couple the two blocks in Eq. (11) are all zero. Each diagonal block is a rigid-monomer Hamiltonian matrix. For this special case, consider the E symmetry block. The E_a and E_b full-dimensional wavefunctions have the same parity, despite the fact that the E_a and E_b Ψ_{inter} factors are, respectively, even and odd. This is simply due to the fact that $\Psi_{\text{inter}}^e(E_a)$ is combined with Ψ_{intra}^e to form the total E_a wavefunction which is even and $\Psi_{\text{inter}}^o(E_b)$ is combined with Ψ_{intra}^o to form the total E_b wavefunction which is also even.

It is interesting to compare with what happens when a case III basis is used. Van der Avoird and co-workers used a case III basis for $\text{NH}_3\text{-He}$ and the same uncoupled primitive basis as in this paper. They derived the $C_{3v}(\text{M})$ symmetry-adapted basis by applying projection operators to a primitive basis function. We find that their $C_{3v}(\text{M})$ symmetry-adapted functions are identical to those we would obtain from our projection operators using a Case II primitive basis, even though the $C_{3v}(\text{M})$ symmetry operations affect the inter-monomer coordinates differently. They further derived a $D_{3h}(\text{M})$ symmetry-adapted basis by applying $E \pm E^*$ to the $C_{3v}(\text{M})$ symmetry-adapted basis because they included an intra-molecular coordinate. We do not include intra-molecular coordinates and therefore this is not necessary

in this paper.

From SAL we obtain irrep-labelled energies and wavefunctions. To understand the energy level pattern and compare with the experimental spectrum, it is very useful to assign K values to each state. Because K is a basis function label, this can be easily done by computing P_K^J as in Ref. 55. P_K^J is obtained by summing squares of eigenvector components over all basis indices except K . It is a measure of the contribution of basis functions labelled by K to a particular ro-vibrational state, See Eq. (15) of Ref. 55. Coriolis coupling between different states labelled with different K is weak for CH₄-H₂O and therefore all states have one dominant K . The K assignment is then compared with experimental K values, which label the lower and upper states of the observed bands. In Ref. 55, we also described methods for assigning rigid rotor quantum numbers j_{K_a, K_c} for H₂O. This is not done in this paper since the rigid rotor quantum numbers for H₂O and CH₄ have been assigned in Ref. 6 for a large number of ro-vibrational states.

VI. A QUADRATURE GRID INVARIANT UNDER C_{3v} OPERATIONS

SAL, which we use within the parity blocks, works only if matrix representations, in the PA basis, of the projection operators commute with the matrix representation of the Hamiltonian operator. [47] Clearly, this is not possible unless the PES is invariant with respect to all the symmetry operations. We find that PES values (the PES of Ref. 3) at a point P and points obtained from P by applying (123) and applying (132) differ by a few 10^{-6} cm⁻¹. This tiny difference can cause SAL not to copy eigenvalues due to the reason given above. [47] We therefore average PES values at the 3 points.

Quadrature error can also cause SAL not to produce copies. [47] In this paper, we therefore use a quadrature grid that is invariant under the C_{3v} operations, as we have done in calculations of CH₃D and CHD₃ vibrational levels[53]. The (123) and (132) operations change γ_B to $\gamma_B \mp 120^\circ$. To ensure that the quadrature grid is invariant under symmetry operations, the first Fourier point for γ_B must be at zero and the number of points must be $N_\phi = 3m$, where m is a positive integer. The latter requirement ensures that the quadrature grid is invariant under (123) and (132).

VII. COMPUTING LINE STRENGTHS

We compute the line strength between two ro-vibrational states. The line strength is required to calculate intensities. Having computed intensities enables one to more reliably match calculated and experimental lines. The line strength is a sum of terms each of which includes the square of an integral of the space-fixed Z dipole component, $\langle \Psi_{i'} | \mu_0^{\text{SF}} | \Psi_i \rangle$. [50] The absolute value of the space-fixed dipole integral is denoted $\langle \mu \rangle$ in the tables. From $\langle \mu \rangle$, one can easily compute the intensity of a line by following Ref.50 . Details of the calculation of the dipole integral are given in Ref.55. Briefly, it is assumed that the only contribution to the dipole moment vector of CH₄-H₂O is the permanent dipole of H₂O (which we set to one) and μ_0^{SF} is written as a linear combination of components along the H₂O MF axes with the combination coefficients being products of Wigner D functions. We know $|\Psi_i\rangle$ as a linear combination of products of Wigner D functions and can therefore compute the integrals. See Eq (14) in Ref. 55.

VIII. COORDINATES AND HAMILTONIAN AND BASIS PARAMETERS

One goal of this study is to compare with the rigid-monomer GENIUSH calculation[5]. GENIUSH uses a DVR basis. The five GENIUSH vibrational angles ($\theta^G, \phi^G, \alpha^G, \beta^G, \gamma^G$) (the superscript G indicates GENIUSH) are essentially the same as our angles, however, their description of the coordinates is not precise in some places. Sarka et al.'s body-fixed(BF) frame depends on three Euler angles, as required by the GENIUSH KEO. They do not clearly define the three Euler angles. It is clear that their first two Euler angles are α and β , because the z axis of their BF frame is the z axis of our DF frame. We deduce that their third Euler angle is α_A , the first Euler angle specifying the orientation of H₂O in the DF frame. The relation between the other two Euler angles we use for H₂O and their angles is: $(\beta_A, \gamma_A) = (0, \theta^G, \phi^G + 90^\circ)$. 90° is added to ϕ^G because Sarka et al.'s MF frame for H₂O has its x -axis perpendicular to the H₂O plane, whereas we have x -axis on the H₂O plane. Their Euler angles for CH₄ ($\alpha^G, \beta^G, \gamma^G$) correspond to our $(\alpha_B - \alpha_A, \beta_B, \gamma_B)$. The relation between Sarka et al.'s and our coordinates is confirmed by calling the MW potential at the equilibrium values given by Sarka et al., and converted to our six angles $(\alpha_A, \beta_A, \gamma_A; \alpha_B, \beta_B, \gamma_B) = (0, 116.19, 90 + 90; 297.46, 113.05, 293.01)$ (in degrees), and

reproducing exactly the value of the PES at equilibrium.

We have located the global minimum and the secondary minimum, in our coordinates, and found the corresponding energies. They are reported in Table I. The secondary minimum (SM) is about 99 cm^{-1} higher than the global minimum (GM). As shown by Sarka et al., the ground state is well localised in the GM. The GM angular coordinates are used to define a cut potential for r_0 , to make a Potential Optimised DVR (PODVR) basis.[56, 57] Note that the Euler angles at equilibrium for CH_4 are not unique because CH_4 has many equivalent wells. For example, there is another GM at $(\alpha_B, \beta_B, \gamma_B) = (62.54^\circ, 113.05^\circ, 66.99^\circ)$.

The KEO of Eq. (2) depends on monomer rotational constants. Usually the best choice is to use experimental rotational constants for the ground state. However, since our goal is to compare with the GENIUSH calculation, we use rotational constants calculated from the masses and structure parameters used in the GENIUSH calculation of Ref. 5.

The structure parameters of CH_4 and H_2O are set to ground state vibrationally averaged values : $r(\text{C-H}) = 1.09912\text{ \AA}$, $r(\text{O-H}) = 0.9716257\text{ \AA}$, $\theta(\text{H-O-H}) = 104.69^\circ$. The original references for these values are given in Refs. 3, 5. From these structure parameters and masses[5], the following rotational constants are obtained: $B = 5.19221\text{ cm}^{-1}$ for CH_4 ; $A = 26.72888$, $B = 9.24512$, $C = 14.13377\text{ cm}^{-1}$ for H_2O . The GENIUSH KEO does not depend on monomer rotational constants. In the GENIUSH calculations, the intra-monomer coordinates are fixed at the above structure parameters and the intermolecular $\mathbf{G}$ matrix is computed by deleting the corresponding rows and columns from the inverse of the full $\mathbf{G}$ and then inverting. The KEO derived this way should be consistent with the KEO we use in which the monomer rotational constants are calculated from the fixed monomer geometry. This is corroborated by the fact that the zero point energy (ZPE) and the first excited vibrational state relative to the ZPE agree to within 0.01 and 0.002 cm^{-1} (Table IX).

The basis functions used in the calculation are defined in Table VII. For r_0 , a cut PODVR is used. Basis 1 is used to compute all levels reported in this paper. With this basis, the levels in the tables are converged to a few 0.001 cm^{-1} , compared to levels computed with larger angular and stretch bases.

IX. ENERGY LEVELS AND COMPARISON WITH GENIUSH

In Table VIII, selected $J = 0$ and $J = 1$ levels on the AOSz05 PES[3] are presented to show the small A/E splittings. The results of the GENIUSH calculation are also included in the table[5]. GENIUSH calculations were done with two basis, SG and LG. SG is a small grid with 21 scaled Legendre PODVR points for β_{CH_4} and LG is a large grid with 101 unscaled Legendre DVR points for β_{CH_4} . The LG basis converges levels better than the SG basis, in particular, the symmetry splittings of LG F levels are smaller than those computed with the SG basis (e.g. the splitting is reduced from 0.04 cm^{-1} to 0.005 cm^{-1} for the F_1^+ level near 36.4 cm^{-1} in Table VIII). The LG basis has 5 times more DVR points. The LG basis is presumably required because of the singularity at $\beta_{\text{CH}_4} = 0, \pi$. To find $T_d(\text{M})$ symmetry labels from the $C_{3v}(\text{M})$ symmetry labels we know, it is important that splittings between levels that should be degenerate be tiny. Representative splittings are those between A and E levels of $C_{3v}(\text{M})$ that correlate with an F level of $T_d(\text{M})$. With the Basis 1 defined in Table VII, these splittings are about 10^{-6} cm^{-1} for all levels up to 100 cm^{-1} . E.g., for the F_1^+ level at $36.413940 \text{ cm}^{-1}$ (See Table VIII), the splitting between the A_2^+ and E_a^+ (or E_b^+) levels is 10^{-6} cm^{-1} and we can safely deduce that the three levels A_2^+ , E_a^+ and E_b^+ are components of the F_1^+ level, as required by the correlation table. The GENIUSH calculation does not take advantage of symmetry. The GENIUSH splittings between levels that should be degenerate are much larger and starting with the GENIUSH levels it is difficult to assign $T_d(\text{M})$ symmetry labels because it is hard to distinguish levels that are close from levels that should be degenerate. For example, the 38th to 43rd $J=1$ levels are composed of one F_1^+ and one F_2^+ level with a separation of 0.0006 cm^{-1} (Table VIII, column 5). We can assign these two levels because our A/E splitting (10^{-6} cm^{-1}) is smaller than the separation of the two levels. GENIUSH cannot assign these two levels because the GENIUSH splittings between components of the two triply degenerate levels is 0.11 and 0.05 cm^{-1} , respectively (Table VIII, column 4). According to our calculation, the F_1^+ state at $30.687439 \text{ cm}^{-1}$ and the F_2^+ state at $30.688042 \text{ cm}^{-1}$ are very close. Encouragingly, one of the GENIUSH F_1^+ components is also very close to one of the F_2^+ , both at 30.588 cm^{-1} . Finally, the order of the E^- level at 36.404 cm^{-1} and the F_1^+ level at 36.414 cm^{-1} was reversed in the LG GENIUSH calculation but was correct in the SG GENIUSH calculation.

Although we and GENIUSH are using essentially the same coordinates, our bases are very different. GENIUSH uses a direct product DVR basis for the 5 vibrational angles to compute $J = 0$ wavefunctions and then makes a direct product ro-vibrational basis from the $J = 0$ wavefunctions and a Wang rotational basis (made from $|JKM\rangle$ functions). On the other hand, we use the PA basis made from the nondirect product basis whose functions are the ξ in Eq. (5). The basis of Eq. (5) is a nondirect product basis because the Wigner bases are themselves nondirect product functions and because of the $K = m_A + m_B$ constraint. Nondirect product bases have the advantage that matrix elements of singular operators in the KEO are finite. [28, 30, 58] If the amplitude of wavefunctions at singularities is not large, then it is possible to compute converged wavefunctions by using a large direct product basis. [59–62] This is true for the same reason that the expansion of an associated Legendre function $\Theta_{\ell,m=1}$ in a very large $\Theta_{\ell,m=0}$ basis can be made accurate almost everywhere. The price one pays for using a direct product basis is that it must be large. For example, in the LG (large grid) basis of GENIUSH, 101 DVR points are needed for the θ^G angle. Our computed $J = 0$, $J = 1$, and $J = 2$ levels on the AOSz05 PES[3] are given in Tables IX, X, XI, XII, and XIII, together with the GENIUSH levels. As seen from Table IX, our vibrational levels and those computed with GENIUSH are close. The differences are smaller than 0.1 cm^{-1} for all the vibrational states below 50 cm^{-1} , but the differences increase at higher energies, and the largest difference for levels reported in Ref. 5 is 0.44 cm^{-1} (LG basis) and 0.61 cm^{-1} (SG basis) for a A_2^- level at 66.6 cm^{-1} . This level is included in Table VIII. Note that in the LG and SG calculations, the position of this level in the ordered list of energies is different. This largest difference is due to the convergence error of the GENIUSH calculation.

The $J = 1$ and $J = 2$ GENIUSH levels[5] are not assigned symmetries. Many GENIUSH levels are given in a range in Tables X to XIII because the degenerate components are not fully converged. Moreover, our A/E splittings are less than 10^{-6} cm^{-1} and those of the GENIUSH calculation are about 0.11 cm^{-1} (with their large grid basis). Despite the fact that the Wigner-basis errors are smaller, the $J = 0$ basis size, 2.97 million for Basis 1, is 20 times smaller than the 60 million LG (large grid) basis of the GENIUSH calculation (counting both parities in both methods). The superior convergence of the Wigner-basis calculation makes it possible to identify missassignments in Ref.5. The missassignments were corrected in Ref.6, by doing a second variational calculation with a large fixed value

of r_0 and calculating overlap integrals. The larger the basis, the larger is the size of the Lanczos vectors, and the spectral range of the Hamiltonian matrix and hence the number of required Lanczos iterations. A large basis is particularly detrimental for GENIUSH because it stores and orthogonalizes all the Lanczos vectors. When spurious eigenvalues are identified using the Cullum and Willoughby test, [63] no orthogonalization is necessary and it is only necessary to store two Lanczos vectors.

Another important difference between the two calculations is the treatment of symmetry. Our strategy using the PA basis and SAL has already been explained. In the GENIUSH calculation, no symmetry is utilized (not even the parity symmetry). In the original paper, [5] it is unclear how symmetry labels are assigned. Some irrep labels can be deduced from degeneracies. However, degeneracies alone can not distinguish between A_1 and A_2 and between F_1 and F_2 levels. In the second GENIUSH paper, irreps are assigned by doing two GENIUSH calculations.

X. COMPARISON WITH THE FAR INFRARED EXPERIMENT

Dore *et al.*[1] measured 13 vibration-rotation-tunnelling bands of $\text{CH}_4\text{-H}_2\text{O}$ in the far infrared (FIR) region, ranging from 18 to 35.5 cm^{-1} . Six of the bands are for $\text{CH}_4\text{-orthoH}_2\text{O}$: $(E)_1$, $(E)_2$, $(A/F)_1$, $(A/F)_3$, $(A/F)_2$, and $(A/F)_4$; and 7 bands are for $\text{CH}_4\text{-paraH}_2\text{O}$: $(E)_3$, $(E)_4$, $(E)_5$, $(A/F)_5$, $(A/F)_6$, $(A/F)_7$, and $(A/F)_8$. These band labels were invented by Dore *et al.* and adopted here. We choose to assign the FIR experimental transitions that link $J = 0$, $J = 1$, and $J = 2$ levels, and compare with experimental results in Tables XIV to XXI, following Ref. 5. With the help of intensities and K assignments, we have identified several new strong bands and corrected some mistakes in Ref. 1. To make a label for a new band, we add a suffix X,Y,Z, $\dots$, to a Dore *et al.* band label that shares the same lower state. Overall we have identified the following new strong bands: $(A/F)_{1b}$, $(A/F)_{3X}$, $(A/F)_{4X}$, $(A/F)_{5X}$, $(A/F)_{6X}$, $(A/F)_{6Y}$, $(A/F)_{8X}$, and $(A/F)_{8Y}$. One important feature of the energy level pattern is the presence of doublets. The doublet splitting can be as small as a few 10^{-6} cm^{-1} . Members of a doublet always have the same K and different parities.

The doublet splitting is smaller when K is larger. The doublet splitting is noticeably larger for $K = 0$ than for $K \neq 0$ because the $K = 0$ splitting is due to potential coupling

whereas the $K \neq 0$ splitting is due to the near degeneracy of $+K$ and $-K$ components and rotational coupling terms. For example, for the $J = 2$ levels in Fig. 1, the Σ doublet splitting is 0.08 cm^{-1} whereas the Π and Σ doublet splittings are 0.007 cm^{-1} and 0.00002 cm^{-1} . There are A_1/A_2 , F_1/F_2 doublets. Doublets occur because the two primitive basis functions in the PA function of Eq. (7) have identical zeroth-order energies.

A. $(E)_1$ and $(E)_2$ bands of $\text{CH}_4\text{-orthoH}_2\text{O}$

$(E)_1$ and $(E)_2$ band transitions are given in Table XIV. The two bands share a common lower state. According to Ref. 6, the two bands correspond to $[2, 1_{01}] \rightarrow [2, 1_{10}]$, where the notation means $[j^M, j_{K_a K_c}^W]$.

B. $(A/F)_1$ and $(A/F)_3$ bands of $\text{CH}_4\text{-orthoH}_2\text{O}$

$(A/F)_1$ and $(A/F)_3$ band transitions are given in Table XV. Fig. 1 is the corresponding energy level diagram and shows the levels and the $R(1)$ lines, as a representative of the band. All the levels are F_1/F_2 doublets. The upper state of $(A/F)_1$ is a Σ doublet. It is an example of a Σ doublet with a larger splitting. In Fig. 1, a Σ doublet is represented with a pair of horizontal bars having a larger gap. $(A/F)_1$, $(A/F)_3$, and $(A/F)_{3X}$ all have two sub-bands, labelled as a and b . $(A/F)_{3X}$ is a new band with strong intensity. Dore *et al.* and Sarka *et al.* do not report one component of the Σ doublet in Fig. 1. We denote the corresponding new band $(A/F)_{1b}$.

C. $(A/F)_2$ band of $\text{CH}_4\text{-orthoH}_2\text{O}$.

$(A/F)_2$ band transitions are given in Table XVI. The upper state of this band is a F_1/F_2 Π doublet and the lower state is a F_1/F_2 Σ doublet.

D. $(A/F)_4$ band of $\text{CH}_4\text{-orthoH}_2\text{O}$.

$(A/F)_4$ band transitions are given in Table XVII. The upper state is an A_1/A_2 Π doublet. $(A/F)_{4X}$ is a new band whose upper state is also an A_1/A_2 Π doublet. $(A/F)_4$ and $(A/F)_{4X}$

share a common lower A_1/A_2 Σ state.

E. $(E)_3$, $(E)_4$ and $(E)_5$ bands of CH_4 -*para* H_2O .

$(E)_3$, $(E)_4$ and $(E)_5$ band transitions are given in Table XVIII. Sarka *et al.*[5] proposed two possible candidates for the $(E)_4$ band. These two bands are labelled as $(E)_4$ and $(E)'_4$ in Table XVIII. They have $J = 2$ upper states at 38.6 and 39.6 cm^{-1} , respectively. Because we assign K values we can determine that the experimental band is the $(E)_4$ band. This is true despite the fact that the $(E)_4$ Obs-Cal error is larger than the $(E)'_4$ Obs-Cal error. The $(E)_4$ band has a Δ upper state, which is what is also observed experimentally. On the other hand, the upper state of the $(E)'_4$ band is a Π state. Additional evidence is obtained from computed intensities. The $(E)'_4$ band intensity is much weaker and falls below our threshold ($\langle|\mu|\rangle > 0.1$) for strong bands. By comparing errors of other bands with those of the $(E)_3$ band, Sarka *et al.* also conclude that the state at 38.6 cm^{-1} is more likely to be the upper state of the observed $(E)_4$ band.

Furthermore, our calculation shows that the upper state of the $(E)_5$ band is a Σ state and it is incorrectly assigned as a Π state by the experimentalists[1]. Dore *et al.* assigned the upper state as a Π state because they did not see the $P(1)$ line[1]. We did find a strong $P(1)$ line at 34.986 cm^{-1} . It must have been missed by the experimentalists. Experimental K assignments are unreliable if not all low- J lines are observed.

F. $(A/F)_5$ band of CH_4 -*para* H_2O .

$(A/F)_5$ and $(A/F)_{5X}$ band transitions are given in Table XIX. $(A/F)_{5X}$ is a new band. The computed intensities of the lines are strong. Its lines are in the range 34.8 to 35.9 cm^{-1} , at the upper end of Dore *et al.*'s experimental spectrum[1] and should be observable. The upper states of both the $(A/F)_5$ and $(A/F)_{5X}$ bands are F_1/F_2 Π doublets.

G. $(A/F)_6$ and $(A/F)_7$ band of CH_4 -*para* H_2O .

$(A/F)_6$, $(A/F)_{6X}$, $(A/F)_{6Y}$, and $(A/F)_7$ band transitions are given in Table XX. $(A/F)_{6X}$ and $(A/F)_{6Y}$ are two strong new bands which should be observable. The lower

state of $(A/F)_7$ is a F_1/F_2 Π doublet and the upper state of $(A/F)_7$ is a F_1/F_2 Δ doublet. Because both lower and upper states are doublets, $(A/F)_7$ is a double band. The a and b sub-bands of $(A/F)_7$ have different upper states, F_1 and F_2 , respectively. The separation between F_1 and F_2 is on the order of 10^{-5} cm^{-1} . The energies of these two states look identical in Table XIX, where 4 digits after the decimal are given, but in Table XII where 6 digits after the decimal are given, the difference between them is noticeable.

H. $(A/F)_8$ band of CH_4 -*para* H_2O .

$(A/F)_8$, and $(A/F)_{8X}$ and $(A/F)_{8Y}$ band transitions are given in Table XXI. $(A/F)_{8X}$ and $(A/F)_{8Y}$ are two new bands. $(A/F)_{8X}$ is interesting because it links the ground state of the global minimum (GM) and the ground state of the secondary minimum (SM). The intensity is surprisingly strong. In many VdW systems, transitions between states associated with the GM and a SM are not observed because the dipole transition moment is usually small (an unfavourable overlap of intermolecular wavefunctions (Franck-Condon factor)). As a result, the GM and SM are usually considered two isomers. The GM to SM transition is unusually intense probably because the wavefunctions in the SM are de-localised. The $(A/F)_{8X}$ band is predicted to be around $34\text{-}35$ cm^{-1} , right at the edge of Dore *et al.*'s experimental range. $(A/F)_{8Y}$ is another band linking the GM and SM, but its upper state is assigned as a stretch state of the SM[5]. Because the $(A/F)_{8X}$ and $(A/F)_{8Y}$ upper states are not doublets, they have no Q-branches, unlike $(A/F)_8$ whose upper state is a A_1/A_2 Π doublet.

XI. COMPARISON WITH MICROWAVE EXPERIMENT

Suenram *et al.*[2] measured microwave transitions of $\text{CH}_4\text{-H}_2\text{O}$ and its isotopologues in a supersonic expansion at a rotational temperature of $\sim 1\text{K}$. For $\text{CH}_4\text{-H}_2\text{O}$, they measured four $K = 0$ (Σ) and six $K = 1$ (Π) bands (two E bands and two double F bands). All these bands have $\Delta K = 0$. All the measured transitions of $\text{CH}_4\text{-H}_2\text{O}$ are given in Table XXII and compared with our calculated values. Guided by Stark effect and nuclear-spin hyperfine measurements, Suenram *et al.*[2] assigned K and symmetries for their bands, see the first column of Table XXII. The experimental assignments are all confirmed by our calculation. In

addition, we can determine the 1 or 2 subscripts on the irrep labels. The agreement between the experimental and calculated transitions is good with the largest difference being 0.0035 cm^{-1} . The two sub-bands of the $F^{\pm}, \Pi$ band have closely spaced pairs of lines. E.g. the two $R(1)$ lines of the F^{-}, Π band are separated by 0.0040 cm^{-1} . Due to the high accuracy of our calculation, these two lines are distinguishable and their separation is calculated to be 0.0048 cm^{-1} . As we see also in the comparison with the FIR experiment, the separation of the doublet lines is more accurately predicted than the lines themselves. As a result, one finds that the Obs - Cal1 values in the last column of Table XXII for these two lines are very close. All the observed MW transitions have strong calculated dipole moment matrix elements. All possible MW transitions between the lowest $J = 0$, $J = 1$ and $J = 2$ levels for each symmetry are observed in the experiment. We also note that some of the lower states are not the lowest for each symmetry, presumably due to imperfect cooling. These are the non-bold numbers in column 6 of Table XXII.

XII. CONCLUSION

The combination of the Brocks et al. KEO, Wigner D basis functions, and SAL is ideal for computing spectra of VdW dimers. It should be used as a first resort. In this paper, we have used the code previously developed for water dimer[25] calculations with rigid monomers to compute ro-vibrational levels of $\text{CH}_4\text{-H}_2\text{O}$. The code is called NNR (Nonlinear-Nonlinear-Rigid) and can be used for calculations on any VdW molecule with two non-linear rigid monomers. The corresponding computer code cannot be used to compute spectra of semi-rigid polyatomic molecules, e.g. methane. For semi-rigid molecules, the Euler coordinates, in terms of which the Brocks et al. KEO is written, are not ideal. For VdW dimers, the Wigner D basis required to obtain converged energy levels and wavefunctions is significantly smaller than the direct product DVR basis would be. This is due in part to being perfectly adapted to dealing with the ineluctable singularities in the KEO. SAL makes it possible to use a simple (not symmetry adapted) basis and nonetheless reduce the cost of the calculation and obtain levels labelled by irreps. For semi-rigid molecules, related ideas can be used with polyspherical coordinates and nondirect product basis functions. Also in that case the nondirect product basis is more efficient than a product DVR. [64] It is also possible to replace Lanczos

with Filter Diagonalisation.[24]

In this paper, we have demonstrated the power of these ideas by applying them to the methane-water VdW complex. We are not the first to compute energy levels of MW, but our calculation is so well converged that we are able to compute very small splittings between doublets of levels with different parities. The accuracy of the converged energies, the calculated transition dipole integrals, the certain irrep labels, and the K assignments enable us to identify some missassignments and new bands that experimentalists should be able to observe. One important new band is A/F_{8X} connecting the ground state of the GM to the ground state of the SM. It is strong and should be observable in Dore et al.'s experimental range. GM and SM are different isomers. Transitions between different isomers, such as the polar and non-polar isomers of NNO dimer, are usually not observed. In methane-water the GM to SM transition is probably strong because the wavefunctions in the SM are de-localised.

XIII. DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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TABLE I: Stationary points on the H₂O-CH₄ PES. GM is the global minimum. SM is the secondary minimum. Distances are in Å and angles are in degrees. Monomer A is H₂O and B is CH₄.

	GM	SM
$(\alpha_A, \beta_A, \gamma_A)$	(0, 116.19, 0)	(0, 22.15, 90)
$(\alpha_B, \beta_B, \gamma_B)$	(0, 7.43, 60)	(60.22, 70.17, 119.34)
r_0	3.4642	3.7729
$V(\text{cm}^{-1})$	-356.68	-257.66

TABLE II: Effect of $C_{3v}(\text{M}) \otimes S_2$ symmetry operations on the angular coordinates of CH₄-H₂O. A is H₂O. B is CH₄. Labels 1 to 4 are for the H atoms of CH₄. For rigid monomers, the effect on the CH₄ angles depends on the atom labelling. Our atom labels for CH₄ (See Fig. S1.) are obtained from those of Table A-14 of Ref. 50 by permuting labels 2 and 3. Labels a and b are for the H atoms of H₂O.

Operator	angles		
E	(α, β)	$(\alpha_A, \beta_A, \gamma_A)$	$(\alpha_B, \beta_B, \gamma_B)$
E^*	$(\pi + \alpha, \pi - \beta)$	$(\pi - \alpha_A, \beta_A, -\gamma_A)$	$(\pi - \alpha_B, \beta_B, -\gamma_B)$
$(23)^*$	$(\pi + \alpha, \pi - \beta)$	$(\pi - \alpha_A, \beta_A, -\gamma_A)$	$(\pi - \alpha_B, \beta_B, -\gamma_B)$
(123)	(α, β)	$(\alpha_A, \beta_A, \gamma_A)$	$(\alpha_B, \beta_B, \gamma_B - 2\pi/3)$
(132)	(α, β)	$(\alpha_A, \beta_A, \gamma_A)$	$(\alpha_B, \beta_B, \gamma_B + 2\pi/3)$
(ab)	(α, β)	$(\alpha_A, \beta_A, \gamma_A + \pi)$	$(\alpha_B, \beta_B, \gamma_B)$

TABLE III: Effect on the primitive basis functions, $|j_A k_A m_A; j_B k_B m_B; JKM\rangle$, of symmetry operations required to apply the projection operators (See Table IV).

Operator	Results
E	$ j_A k_A m_A; j_B k_B m_B; JKM\rangle$
E^*	$(-1)^{J+k_A+k_B} j_A \bar{k}_A \bar{m}_A; j_B \bar{k}_B \bar{m}_B; J\bar{K}\bar{M}\rangle$
$(23)^*$	$(-1)^{J+k_A+k_B} j_A \bar{k}_A \bar{m}_A; j_B \bar{k}_B \bar{m}_B; J\bar{K}\bar{M}\rangle$
(123)	$e^{i\frac{2\pi}{3}k_B} j_A k_A m_A; j_B k_B m_B; JKM\rangle$
(132)	$e^{-i\frac{2\pi}{3}k_B} j_A k_A m_A; j_B k_B m_B; JKM\rangle$
(ab)	$(-1)^{k_A} j_A k_A m_A; j_B k_B m_B; JKM\rangle$

TABLE IV: Definition of $C_{3v}(M)$ and S_2 projection operators and their effect on the PA basis

Projection operators	effect on $u_{j_A k_A m_A; j_B k_B m_B; K}^{JMP}$	
$P^{A_1} = (1/6)[E + (123) + (132)][E + (23)^*]$	$u_{j_A k_A m_A; j_B k_B m_B; K}^{JMP}$	$k_B = 0(\text{mod } 3) \text{ and } P = 0$
$P^{A_2} = (1/6)[E + (123) + (132)][E - (23)^*]$	$u_{j_A k_A m_A; j_B k_B m_B; K}^{JMP}$	$k_B = 0(\text{mod } 3) \text{ and } P = 1$
$P^{E_a} = (1/6)[2E - (123) - (132)][E + (23)^*]$	$u_{j_A k_A m_A; j_B k_B m_B; K}^{JMP}$	$k_B \neq 0(\text{mod } 3) \text{ and } P = 0$
$P^{E_b} = (1/6)[2E - (123) - (132)][E - (23)^*]$	$u_{j_A k_A m_A; j_B k_B m_B; K}^{JMP}$	$k_B \neq 0(\text{mod } 3) \text{ and } P = 1$
$P^+ = (1/2)[E + (ab)]$	$u_{j_A k_A m_A; j_B k_B m_B; K}^{JMP}$	$k_A = \text{even}$
$P^- = (1/2)[E - (ab)]$	$u_{j_A k_A m_A; j_B k_B m_B; K}^{JMP}$	$k_A = \text{odd}$

TABLE V: $C_{3v}(\text{M}) \otimes S_2$ symmetry of the PA basis $u_{j_A k_A m_A; j_B k_B m_B; K}^{JMP}$. The bottom half of the table gives the correlation between $T_d(\text{M}) \otimes S_2$ and its subgroup $C_{3v}(\text{M}) \otimes S_2$.

P	k_A	k_B	$C_{3v}(\text{M}) \otimes S_2$
even parity	$k_A = \text{even}$	$k_B = 0(\text{mod } 3)$	A_1^+
	$k_A = \text{odd}$	$k_B = 0(\text{mod } 3)$	A_1^-
	$k_A = \text{even}$	$k_B \neq 0(\text{mod } 3)$	E_a^+
	$k_A = \text{odd}$	$k_B \neq 0(\text{mod } 3)$	E_a^-
odd parity	$k_A = \text{even}$	$k_B = 0(\text{mod } 3)$	A_2^+
	$k_A = \text{odd}$	$k_B = 0(\text{mod } 3)$	A_2^-
	$k_A = \text{even}$	$k_B \neq 0(\text{mod } 3)$	E_b^+
	$k_A = \text{odd}$	$k_B \neq 0(\text{mod } 3)$	E_b^-
$T_d(\text{M}) \otimes S_2$	$C_{3v}(\text{M}) \otimes S_2$		
A_1^+	A_1^+		
A_2^+	A_2^+		
E^+	E^+		
F_1^+	$A_2^+ + E^+$		
F_2^+	$A_1^+ + E^+$		
A_1^-	A_1^-		
A_2^-	A_2^-		
E^-	E^-		
F_1^-	$A_2^- + E^-$		
F_2^-	$A_1^- + E^-$		

TABLE VI: Feasible molecular symmetry group G_{48} for the $\text{CH}_4\text{-H}_2\text{O}$ dimer. This table is the same as Table A-29 of Ref. 50 except that for the 25th to 48th symmetry operations, E^* is replaced by (ab). TW is “This Work”. Ref. 5 is the corresponding irrep of Ref. 5.

TW	Ref. 5	E	(123)	(14)(23)	(1423)*	(23)*	(ab)	(123)(ab)	(14)(23)(ab)	(1423)*(ab)	(23)*(ab)
		1	8	3	6	6	1	8	3	6	6
A_1^+	A_1^+	1	1	1	1	1	1	1	1	1	1
A_2^+	A_2^+	1	1	1	-1	-1	1	1	1	-1	-1
E^+	E^+	2	-1	2	0	0	2	-1	2	0	0
F_1^+	F_1^+	3	0	-1	1	-1	3	0	-1	1	-1
F_2^+	F_2^+	3	0	-1	-1	1	3	0	-1	-1	1
A_1^-	A_2^-	1	1	1	1	1	-1	-1	-1	-1	-1
A_2^-	A_1^-	1	1	1	-1	-1	-1	-1	-1	1	1
E^-	E^-	2	-1	2	0	0	-2	1	-2	0	0
F_1^-	F_2^-	3	0	-1	1	-1	-3	0	1	-1	1
F_2^-	F_1^-	3	0	-1	-1	1	-3	0	1	1	-1

TABLE VII: Basis set paramters. N_{r_0} is the number of PODVR DVR basis for stretch coordinate r_0 . The PODVR functions are computed with a cut potential in the range $[4.0, 20.0]$ Bohr for r_0 . $j_{\max}$ is the maximum value of (j_X, k_X, m_X) with $X = A$ and B . N_θ and N_ϕ are the numbers of Gauss-Legendre quadrature points for β_X and Fourier points for α_X and γ_X . N_{bas} is the number of even-parity basis functions. 1 M = 1 million.

Basis	N_{r_0}	$j_{\max}$	N_θ	N_ϕ	N_{bas}
Basis 1	15	12	15	30	2.97 M
Basis 2	15	14	15	30	6.08 M

TABLE VIII: Comparison of selected CH₄-H₂O levels (in cm⁻¹) with all the degenerate components. $J = 0$ levels of CH₄-H₂O up to 50 cm⁻¹, relative to the ZPE (zero point energy) except for the ZPE which is relative to the bottom of the well. TW is from this work. GENIUSH is from Ref. 5. $\Delta = \text{GENIUSH(LG)} - \text{TW}$. SG is for small grid with 21 scaled Legendre PODVR points for β_{CH_4} and LG is for large grid with 101 unscaled Legendre DVR points for β_{CH_4} . Sym2 are the subgroup $C_{3v}(\text{M}) \otimes S_2$ symmetry labels used in the calculation. Sym1 are the full MS group G_{48} symmetry labels derived from Sym2. The labels $J0.n$ and $J1.n$ in the first two columns indicate levels with $J = 0$ and 1 where $n = 1, 2, \dots$ labels the levels based on their energy order.

Label(SG)	Label(LG)	Geniush(SG)	Geniush(LG)	TW	Sym1	Sym2	Δ
J0.1	J0.1	206.792	206.801	206.810000	A_1^+	A_1^+	-0.01
J0.2	J0.2	4.763	4.763	4.765104	F_2^+	A_1^+	0.00
J0.3	J0.3	4.763	4.764	4.765104		E_a^+	0.00
J0.4	J0.4	4.765	4.764	4.765104		E_b^+	0.00
J0.21	J0.24	36.257	36.397	36.404185	E^-	E_a^-	-0.01
J0.22	J0.25	36.257	36.397	36.404185		E_b^-	-0.01
J0.23	J0.21	36.323	36.317	36.413940	F_1^+	A_2^+	-0.10
J0.24	J0.22	36.365	36.317	36.413941		E_a^+	-0.10
J0.25	J0.23	36.365	36.322	36.413941		E_b^+	-0.09
J0.63	J0.66	65.992	66.156	66.596896	A_2^-	A_2^-	-0.44
	J1.1		0.289	0.289296	A_2^+	A_2^+	0.00
	J1.2		5.044	5.046731	F_1^+	A_2^+	0.00
	J1.3		5.044	5.046731		E_a^+	0.00
	J1.4		5.045	5.046731		E_b^+	0.00
	J1.38		30.474	30.687439	F_1^+	A_2^+	-0.21
	J1.39		30.474	30.687439		E_a^+	-0.21
	J1.40		30.588	30.687439		E_b^+	-0.10
	J1.41		30.588	30.688042	F_2^+	A_1^+	-0.10
	J1.42		30.633	30.688042		E_a^+	-0.06
	J1.43		30.633	30.688042		E_b^+	-0.06

TABLE IX: $J = 0$ levels of $\text{CH}_4\text{-H}_2\text{O}$ up to 50 cm^{-1} , relative to the ZPE (zero point energy) except for the ZPE which is relative to the bottom of the well. TW is from this work. GENIUSH is from Ref. 5. “Sym” for GENIUSH is the symmetry label, taken from Table 18 of Ref. 7 which corrected several symmetry label mistakes in Ref. 5. $\Delta = \text{GENIUSH(LG)} - \text{TW}$. The symmetry of levels marked by * are mis-assigned in Ref. 5, but corrected in Ref. 6 and Ref. 7. LG and SG are the “large grid” and “small grid” GENIUSH calculations[5]. Desc. describes the vibrational state. ZPV means zero point vibration. Bands lists the bands that involve the state of the row. If a band is in boldface, it means that the state is the lower state of that band.

TW	Sym(TW)	GENIUSH			Δ	Desc.	Bands
		SG	LG	Sym			
206.810	A_1^+	206.792	206.801	A_1^+	-0.009	ZPV(GM)	(A/F)₈ , (A/F)_{8X} , (A/F)_{8Y}
4.765	F_2^+	4.763	4.763	F_2^{+*}	-0.002	ZPV(GM)	(A/F)₅ , (A/F)_{5X}
6.993	A_1^-	6.930	6.934	A_2^-	-0.059	ZPV(GM)	(A/F)₄
11.253	F_2^-	11.177	11.190	F_1^{-*}	-0.063	ZPV(GM)	(A/F)₂
29.034	F_2^+	28.919	29.001	F_2^+	-0.033	ZPV(GM)	$(A/F)_{6X}$
32.636	F_2^-	32.600	32.630	F_1^-	-0.006	ZPV(GM)	$\left. \vphantom{\begin{matrix} (A/F)_{6X} \\ (A/F)_{6Y} \end{matrix}} \right\} (A/F)_1$
32.710	F_1^-	32.701	32.705	F_2^{-*}	-0.005	ZPV(GM)	
34.413	A_1^+	34.407	34.405	A_1^+	-0.008	ZPV(SM)	$(A/F)_{8X}$
35.920	E^+	35.740	35.880	E^+	-0.040	ZPV(GM)	$(E)_3$
36.404	E^-	36.365	36.397	E^-	-0.007	ZPV(GM)	$(E)_1$
36.414	F_1^+	36.257	36.317	F_1^{+*}	-0.097	ZPV(GM)	$(A/F)_6$
41.186	F_2^+	41.102	41.104	F_2^{+*}	-0.082		$(A/F)_{6Y}$
45.976	F_2^-	45.766	45.916	F_1^-	-0.060		
47.290	E^-	47.156	47.253	E^-	-0.037		
48.096	E^+	47.966	48.000	E^+	-0.096		$(E)_5$
48.706	A_1^+	48.672	48.685	A_1^+	-0.021	Str(GM)	$(A/F)_{8Y}$

TABLE X: $J = 1$ levels of $\text{CH}_4\text{-paraH}_2\text{O}$ up to 50 cm^{-1} , relative to the ZPE. TW is from this work. GENIUSH is from Ref. 5 with the “large grid” basis. $\Delta = \text{GENIUSH} - \text{TW}$. GENIUSH F levels are given in a range. The lowest F level is used to compute Δ . Levels are given to given six digits after the decimal to reveal the splittings between F_1 and F_2 levels, and between A_1 and A_2 levels. If a band is in boldface, it means that the state is the lower state of that band.

TW	Sym(TW)	K	GENIUSH	Δ	Bands
0.289296	A_2^+	0	0.289	0.000	(A/F)₈ , (A/F) _{8X} , (A/F) _{8Y}
5.046731	F_1^+	0	5.044- 5.045	-0.003	(A/F) ₅ , (A/F) _{5X}
7.911936	F_2^+	1	7.905- 7.911	-0.007	} (A/F) ₆ , (A/F) _{6X} , (A/F) _{6Y} , (A/F) ₇
7.915663	F_1^+	1	7.911- 7.915	-0.005	
13.110019	E^+	1	13.113	0.003	(E) ₃ , (E) ₄ , (E) ₄ ', (E) ₅
29.305215	F_1^+	0	29.189-29.209	-0.116	(A/F) _{6X}
29.559623	A_2^+	1	29.427	-0.133	} (A/F) ₈
29.565456	A_1^+	1	29.433	-0.132	
30.687439	F_1^+	1	30.474-30.588	-0.213	} (A/F) ₅
30.688042	F_2^+	1	30.588-30.633	-0.100	
34.681064	A_2^+	0	34.675	-0.006	(A/F) _{8X}
36.185723	E^+	0	36.007-36.007	-0.179	(E) ₃
36.699426	F_2^+	0	36.609-36.649	-0.090	(A/F) ₆
39.016179	E^+	1	38.926-38.926	-0.090	(E) ₄ '
40.422287	F_1^+	1	40.331-40.376	-0.091	} (A/F) _{5X}
40.423730	F_2^+	1	40.376-40.380	-0.048	
41.465432	F_1^+	0	41.381-41.404	-0.084	(A/F) _{6Y}
48.377330	E^+	0	48.247-48.247	-0.130	(E) ₅
48.981169	A_2^+	0	48.946	-0.035	(A/F) _{8Y}
49.290315	F_2^+	1	49.058-49.060	-0.232	} (A/F) ₁₀
49.295920	F_1^+	1	49.065-49.266	-0.231	

TABLE XI: $J = 1$ levels of CH_4 -*ortho* H_2O up to 50 cm^{-1} , relative to the ZPE. See the caption of Table X ($J = 1$ table) for more information.

TW	Sym(TW)	K	GENIUSH	Δ	Bands
7.281957	A_2^-	1	7.219	-0.063	$(\mathbf{A}/\mathbf{F})_4, (\mathbf{A}/\mathbf{F})_{4\mathbf{x}}$
11.535235	F_1^-	0	11.457-11.475	-0.078	$(\mathbf{A}/\mathbf{F})_2$
14.614084	F_2^-	1	14.543-14.552	-0.071	$\left\{ (\mathbf{A}/\mathbf{F})_1, (\mathbf{A}/\mathbf{F})_3, (\mathbf{A}/\mathbf{F})_{3\mathbf{x}} \right\}$
14.616513	F_1^-	1	14.554-14.555	-0.063	
19.394275	E^-	1	19.329	-0.065	$(\mathbf{E})_1, (\mathbf{E})_2$
26.361163	A_1^-	1	26.361	0.000	$\left\{ (A/F)_4 \right\}$
26.363708	A_2^-	1	26.363	-0.001	
29.761713	F_2^-	1	29.729-29.760	-0.033	$\left\{ (A/F)_2 \right\}$
29.763934	F_1^-	1	29.760-29.765	-0.004	
32.924699	F_1^-	0	32.888-32.902	-0.037	$\left\{ (A/F)_1 \right\}$
33.000375	F_2^-	0	32.991-32.998	-0.009	
36.688858	E^-	0	36.542-36.542	-0.147	$(E)_1$
43.061413	A_2^-	1	42.998	-0.063	$\left\{ (A/F)_{4\mathbf{x}} \right\}$
43.064914	A_1^-	1	43.001	-0.064	
44.958917	F_1^-	1	44.728-44.809	-0.231	$\left\{ \right\}$
44.981071	F_2^-	1	44.809-44.933	-0.172	
46.280583	F_1^-	0	46.071-46.133	-0.210	
46.614840	E^-	1	46.568	-0.047	$(E)_6$
47.573736	E^-	0	47.440	-0.134	

TABLE XII: $J = 2$ levels of $\text{CH}_4\text{-}para\text{H}_2\text{O}$ up to 50 cm^{-1} , relative to the ZPE. See the caption of Table X ($J = 1$ table) for more information.

TW	Sym(TW)	K	GENIUSH	Δ	Bands
0.867790	A_1^+	0	0.867	-0.001	$(\mathbf{A}/\mathbf{F})_8, (\mathbf{A}/\mathbf{F})_{8X}, (\mathbf{A}/\mathbf{F})_{8Y}$
5.609971	F_2^+	0	5.605- 5.607	-0.005	$(\mathbf{A}/\mathbf{F})_5, (\mathbf{A}/\mathbf{F})_{5X}$
8.491895	F_1^+	1	8.485- 8.490	-0.007	$\left. \begin{array}{l} (\mathbf{A}/\mathbf{F})_6, (\mathbf{A}/\mathbf{F})_{6X}, (\mathbf{A}/\mathbf{F})_{6Y}, (\mathbf{A}/\mathbf{F})_7 \end{array} \right\}$
8.502992	F_2^+	1	8.497- 8.501	-0.006	
13.680007	E^+	1	13.682	0.002	$(\mathbf{E})_3, (\mathbf{E})_4, (\mathbf{E})'_4, (\mathbf{E})_5$
23.326533	E^+	2	23.320	-0.007	$\left. \begin{array}{l} (A/F)_{10} \end{array} \right\}$
26.380042	F_2^+	2	26.374-26.375	-0.006	
26.380056	F_1^+	2	26.375-26.388	-0.005	
29.848228	F_2^+	0	29.730-29.752	-0.118	$(A/F)_{6X}$
30.127980	A_1^+	1	29.995	-0.133	$\left. \begin{array}{l} (A/F)_8 \end{array} \right\}$
30.145469	A_2^+	1	30.012	-0.133	
31.255907	F_2^+	1	31.043-31.157	-0.213	$\left. \begin{array}{l} (A/F)_5 \end{array} \right\}$
31.257887	F_1^+	1	31.157-31.202	-0.101	
35.217648	A_1^+	0	35.210	-0.008	$(A/F)_{8X}$
36.717787	E^+	0	36.540	-0.178	$(E)_3$
37.270211	F_1^+	0	37.180-37.217	-0.090	$(A/F)_6$
37.645069	F_2^+	2	37.537-37.546	-0.108	$\left. \begin{array}{l} (A/F)_7 \end{array} \right\}$
37.645145	F_1^+	2	37.546-37.564	-0.099	
38.648019	E^+	2	38.531	-0.117	$(E)_4$
39.597050	E^+	1	39.505	-0.092	$(E)'_4$
40.973410	F_2^+	1	40.883-40.928	-0.045	$\left. \begin{array}{l} (A/F)_{5X} \end{array} \right\}$
40.977788	F_1^+	1	40.928-40.933	-0.050	
42.024881	F_2^+	0	41.939-41.963	-0.086	$(A/F)_{6Y}$
48.939213	E^+	0	48.808	-0.131	$(E)_5$
49.531160	A_1^+	0	49.496	-0.035	$(A/F)_{8Y}$
49.833976	F_1^+	1	49.603-49.606	-0.231	$\left. \begin{array}{l} (A/F)_{10} \end{array} \right\}$
49.850668	F_2^+	1	49.620-49.814	-0.231	

TABLE XIII: $J = 2$ levels of $\text{CH}_4\text{-orthoH}_2\text{O}$ up to 50 cm^{-1} , relative to the ZPE. See the caption of Table X ($J = 1$ table) for more information.

TW	Sym(TW)	K	GENIUSH	Δ	Bands
7.859400	A_1^-	0	7.796	-0.063	$(\mathbf{A}/\mathbf{F})_4, (\mathbf{A}/\mathbf{F})_{4X}$
12.099087	F_2^-	0	12.019-12.039	-0.080	$(\mathbf{A}/\mathbf{F})_2$
15.192120	F_1^-	1	15.120-15.130	-0.072	$\left. \begin{array}{l} (\mathbf{A}/\mathbf{F})_1, (\mathbf{A}/\mathbf{F})_3, (\mathbf{A}/\mathbf{F})_{3X} \end{array} \right\}$
15.199349	F_2^-	1	15.136-15.137	-0.063	
19.961882	E^-	1	19.895	-0.067	$(\mathbf{E})_1, (\mathbf{E})_2$
26.938144	A_2^-	1	26.937	-0.001	$\left. \begin{array}{l} (A/F)_4 \end{array} \right\}$
26.945777	A_1^-	1	26.944	-0.002	
29.726527	E^-	2	29.662	-0.065	$(\mathbf{E})_6$
30.329443	F_1^-	1	30.294-30.328	-0.035	$\left. \begin{array}{l} (A/F)_2 \end{array} \right\}$
30.336107	F_2^-	1	30.328-30.336	-0.008	
32.832581	F_2^-	2	32.764-32.770	-0.069	$\left. \begin{array}{l} (A/F)_{3X} \end{array} \right\}$
32.832586	F_1^-	2	32.770-32.788	-0.063	
33.502276	F_2^-	0	33.464-33.480	-0.038	$\left. \begin{array}{l} (A/F)_1 \end{array} \right\}$
33.580791	F_1^-	0	33.571-33.578	-0.010	
34.191165	F_1^-	2	34.185-34.187	-0.006	$\left. \begin{array}{l} (A/F)_3 \end{array} \right\}$
34.191180	F_2^-	2	34.187-34.188	-0.004	
37.258091	E^-	0	37.111	-0.147	$(E)_1$
37.571748	E^-	2	37.479	-0.093	$(E)_2$
43.603320	A_1^-	1	43.539	-0.064	$\left. \begin{array}{l} (A/F)_{4X} \end{array} \right\}$
43.613832	A_2^-	1	43.550	-0.064	
45.476624	F_2^-	1	45.246-45.341	-0.231	$\left. \begin{array}{l} \end{array} \right\}$
45.540479	F_1^-	1	45.341-45.477	-0.199	
46.887791	F_2^-	0	46.677-46.741	-0.211	
47.181826	E^-	1	47.132	-0.050	$(E)_6$
48.141157	E^-	0	48.009	-0.132	

TABLE XIV: $(E)_1$ and $(E)_2$ bands of $\text{CH}_4\text{-orthoH}_2\text{O}$. Cal1 = $E' - E''$. Cal2 is the GENIUSH result from Ref. 5. Energies are in cm^{-1} except for those noted otherwise.

$J', K' \leftarrow J'', K''$	Obs[MHz]	Obs	$E'(\text{sym})$	$E''(\text{sym})$	Cal1	Cal2	$\langle\mu\rangle$	Obs - Cal1
Expt. (Ref. 1): Table III, $(E)_1, \Sigma \leftarrow \Pi$ band								
$1, 0 \leftarrow 2, 1$	524254.1	17.4872	$36.6889(E^-)$	$19.9619(E^-)$	16.7270	16.8	0.480	0.7602
$0, 0 \leftarrow 1, 1$	532812.0	17.7727	$36.4042(E^-)$	$19.3943(E^-)$	17.0099	17.0	0.392	0.7628
$2, 0 \leftarrow 2, 1$	541344.3	18.0573	$37.2581(E^-)$	$19.9619(E^-)$	17.2962	17.3	0.625	0.7611
$1, 0 \leftarrow 1, 1$	541359.5	18.0578	$36.6889(E^-)$	$19.3943(E^-)$	17.2946	17.3	0.480	0.7632
$2, 0 \leftarrow 1, 1$	558451.2	18.6279	$37.2581(E^-)$	$19.3943(E^-)$	17.8638	17.9	0.271	0.7641
Expt. (Ref. 1): Table III, $(E)_2, \Delta \leftarrow \Pi$ band								
$2, 2 \leftarrow 2, 1$	542744.8	18.1040	$37.5717(E^-)$	$19.9619(E^-)$	17.61	17.7	0.512	0.4942
$2, 2 \leftarrow 1, 1$	559850.8	18.6746	$37.5717(E^-)$	$19.3943(E^-)$	18.18	18.2	0.694	0.4972

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TABLE XV: $(A/F)_1$ and $(A/F)_3$ bands of CH_4 -*ortho* H_2O . See the caption of Table XIV for more information.

$J', K' \leftarrow J'', K''$	Obs[MHz]	Obs	E' (sym)	E'' (sym)	Cal1	Cal2	$\langle\mu\rangle$	Obs - Cal1
Expt. (Ref. 1): Table IV, $(A/F)_{1a}$, $\Sigma \leftarrow \Pi$ band								
$1, 0 \leftarrow 2, 1$	529495.8	17.6621	$33.0004(F_2^-)$	$15.1921(F_1^-)$	17.8083	17.8	0.482	-0.1462
$0, 0 \leftarrow 1, 1$	538189.8	17.9521	$32.6359(F_2^-)$	$14.6165(F_1^-)$	18.0194	18.1	0.407	-0.0673
$2, 0 \leftarrow 2, 1$	546715.2	18.2365	$33.5023(F_2^-)$	$15.1921(F_1^-)$	18.3102	18.4	0.646	-0.0737
$1, 0 \leftarrow 1, 1$	546831.5	18.2403	$33.0004(F_2^-)$	$14.6165(F_1^-)$	18.3839	18.4	0.480	-0.1436
$2, 0 \leftarrow 1, 1$	564291.7	18.8227	$33.5023(F_2^-)$	$14.6165(F_1^-)$	18.8858	19.0	0.282	-0.0631
$(A/F)_{1b}$, $\Sigma \leftarrow \Pi$ band (new)								
$1, 0 \leftarrow 2, 1$			$32.9247(F_1^-)$	$15.1993(F_2^-)$	17.7254		0.500	
$0, 0 \leftarrow 1, 1$			$32.7101(F_1^-)$	$14.6141(F_2^-)$	18.0960		0.393	
$1, 0 \leftarrow 1, 1$			$32.9247(F_1^-)$	$14.6141(F_2^-)$	18.3106		0.498	
$2, 0 \leftarrow 2, 1$			$33.5808(F_1^-)$	$15.1993(F_2^-)$	18.3815		0.620	
$2, 0 \leftarrow 1, 1$			$33.5808(F_1^-)$	$14.6141(F_2^-)$	18.9667		0.275	
Expt. (Ref. 1): Table IV, $(A/F)_{3a}$, $\Delta \leftarrow \Pi$ band								
$2, 2 \leftarrow 2, 1$	564637.3	18.8343	$34.1912(F_2^-)$	$15.1921(F_1^-)$	18.9991	19.1	0.464	-0.1648
$2, 2 \leftarrow 1, 1$	581971.4	19.4125	$34.1912(F_2^-)$	$14.6165(F_1^-)$	19.5747	19.6	0.624	-0.1622
Expt. (Ref. 1): Table IV, $(A/F)_{3b}$, $\Delta \leftarrow \Pi$ band								
$2, 2 \leftarrow 2, 1$	564437.7	18.8276	$34.1912(F_1^-)$	$15.1993(F_2^-)$	18.9919	19.1	0.466	-0.1643
$2, 2 \leftarrow 1, 1$	582013.5	19.4139	$34.1912(F_1^-)$	$14.6141(F_2^-)$	19.5771	19.6	0.623	-0.1632
$(A/F)_{3Xa}$, $\Delta \leftarrow \Pi$ band (new)								
$2, 2 \leftarrow 2, 1$			$32.8326(F_2^-)$	$15.1921(F_1^-)$	17.6405		0.201	
$2, 2 \leftarrow 1, 1$			$32.8326(F_2^-)$	$14.6165(F_1^-)$	18.2161		0.273	
$(A/F)_{3Xb}$, $\Delta \leftarrow \Pi$ band (new)								
$2, 2 \leftarrow 2, 1$			$32.8326(F_1^-)$	$15.1993(F_2^-)$	17.6333		0.272	
$2, 2 \leftarrow 1, 1$			$32.8326(F_1^-)$	$14.6141(F_2^-)$	18.2185		0.205	

TABLE XVI: $(A/F)_2$ band of CH_4 -*ortho* H_2O . See the caption of Table XIV for more information.

$J', K' \leftarrow J'', K''$	Obs[MHz]	Obs	E' (sym)	E'' (sym)	Cal1	Cal2	$\langle\mu\rangle$	Obs - Cal1
Expt. (Ref. 1): Table V, $(A/F)_2$, $\Pi \leftarrow \Sigma$ band								
$1, 1 \leftarrow 2, 0$	536931.0	17.9101	$29.7639(F_1^-)$	$12.0991(F_2^-)$	17.6648	17.7	0.400	0.24532
$2, 1 \leftarrow 2, 0$	553883.6	18.4756	$30.3294(F_1^-)$	$12.0991(F_2^-)$	18.2303	18.3	0.891	0.24533
$1, 1 \leftarrow 1, 0$	553888.4	18.4757	$29.7617(F_2^-)$	$11.5352(F_1^-)$	18.2265	18.3	0.691	0.24927
$1, 1 \leftarrow 0, 0$	562445.5	18.7612	$29.7639(F_1^-)$	$11.2533(F_2^-)$	18.5106	18.6	0.563	0.25066
$2, 1 \leftarrow 1, 0$	571055.5	19.0484	$30.3361(F_2^-)$	$11.5352(F_1^-)$	18.8009	18.9	0.689	0.24751

TABLE XVII: $(A/F)_4$ band of CH_4 -*ortho* H_2O . See the caption of Table XIV for more information.

$J', K' \leftarrow J'', K''$	Obs[MHz]	Obs	E' (sym)	E'' (sym)	Cal1	Cal2	$\langle\mu\rangle$	Obs - Cal1
Expt. (Ref. 1): Table VI, $(A/F)_4$, $\Pi \leftarrow \Sigma$ band								
$1, 1 \leftarrow 2, 0$	548506.7	18.2962	$26.3637(A_2^-)$	$7.8594(A_1^-)$	18.5043	18.6	0.398	-0.2081
$2, 1 \leftarrow 2, 0$	565694.1	18.8695	$26.9381(A_2^-)$	$7.8594(A_1^-)$	19.0787	19.1	0.885	-0.2092
$1, 1 \leftarrow 1, 0$	565794.7	18.8729	$26.3612(A_1^-)$	$7.2820(A_2^-)$	19.0792	19.1	0.686	-0.2063
$1, 1 \leftarrow 0, 0$	574574.9	19.1658	$26.3637(A_2^-)$	$6.9932(A_1^-)$	19.3705	19.4	0.558	-0.2047
$2, 1 \leftarrow 1, 0$	583344.0	19.4583	$26.9458(A_1^-)$	$7.2820(A_2^-)$	19.6638	19.7	0.681	-0.2055
$(A/F)_{4X}$, $\Pi \leftarrow \Sigma$ band (new)								
$1, 1 \leftarrow 2, 0$			$43.0614(A_2^-)$	$7.8594(A_1^-)$	35.2020		0.156	
$2, 1 \leftarrow 2, 0$			$43.6138(A_2^-)$	$7.8594(A_1^-)$	35.7544		0.343	
$1, 1 \leftarrow 1, 0$			$43.0649(A_1^-)$	$7.2820(A_2^-)$	35.7829		0.266	
$1, 1 \leftarrow 0, 0$			$43.0614(A_2^-)$	$6.9932(A_1^-)$	36.0682		0.215	
$2, 1 \leftarrow 1, 0$			$43.6033(A_1^-)$	$7.2820(A_2^-)$	36.3213		0.261	

TABLE XVIII: $(E)_3$, $(E)_4$ and $(E)_5$ bands of CH_4 -*para* H_2O . See the caption of Table XIV for more information.

$J', K' \leftarrow J'', K''$	Obs[MHz]	Obs	E' (sym)	E'' (sym)	Cal1	Cal2	$\langle\mu\rangle$	Obs - Cal1
Expt. (Ref. 1): Table VII, $(E)_3$, $\Sigma \leftarrow \Pi$ band								
$1, 0 \leftarrow 2, 1$	723657.8	24.1386	$36.1857(E^+)$	$13.6800(E^+)$	22.5057	22.3	0.367	1.6329
$0, 0 \leftarrow 1, 1$	732385.1	24.4297	$35.9198(E^+)$	$13.1100(E^+)$	22.8098	22.6	0.304	1.6199
$2, 0 \leftarrow 2, 1$	740443.2	24.6985	$36.7178(E^+)$	$13.6800(E^+)$	23.0378	22.9	0.481	1.6607
$1, 0 \leftarrow 1, 1$	740778.1	24.7097	$36.1857(E^+)$	$13.1100(E^+)$	23.0757	22.9	0.374	1.6340
$2, 0 \leftarrow 1, 1$	757561.5	25.2695	$36.7178(E^+)$	$13.1100(E^+)$	23.6078	23.4	0.218	1.6617
Expt. (Ref. 1): Table VII, $(E)_4$, $\Delta \leftarrow \Pi$ band								
$2, 2 \leftarrow 2, 1$	821483.9	27.4018	$38.6480(E^+)$	$13.6800(E^+)$	24.9680	24.8	0.460	2.4338
$2, 2 \leftarrow 1, 1$	838603.8	27.9728	$38.6480(E^+)$	$13.1100(E^+)$	25.5380	25.4	0.628	2.4348
Expt. (Ref. 1): Table VII, $(E)_4'$, $\Pi \leftarrow \Pi$ band								
$2, 1 \leftarrow 2, 1$	821483.9	27.4018	$39.5971(E^+)$	$13.6800(E^+)$	25.9171	24.8	0.071	1.4847
$2, 1 \leftarrow 1, 1$	838603.8	27.9728	$39.5971(E^+)$	$13.1100(E^+)$	26.4871	25.4	0.033	1.4857
$2, 1 \leftarrow 1, 1$			$39.0162(E^+)$	$13.6800(E^+)$	25.9171		0.032	
$2, 1 \leftarrow 1, 1$			$39.0162(E^+)$	$13.1100(E^+)$	26.4871		0.032	
Expt. (Ref. 1): Table VII, $(E)_5$, $\Sigma \leftarrow \Pi$ band*								
$2, 0 \leftarrow 2, 1$	1057801.7	35.2845	$48.9392(E^+)$	$13.6800(E^+)$	35.2592	35.1	0.468	0.0253
$1, 0 \leftarrow 1, 1$	1057943.1	35.2892	$48.3773(E^+)$	$13.1100(E^+)$	35.2673	35.1	0.363	0.0219
$2, 0 \leftarrow 1, 1$	1074920.4	35.8555	$48.9392(E^+)$	$13.1100(E^+)$	35.8292	35.7	0.210	0.0263
$0, 0 \leftarrow 1, 1$			$48.0963(E^+)$	$13.1100(E^+)$	34.9863		0.295	

* The upper state symmetry of this band was mis-assigned as Π in Ref. 1.

TABLE XIX: $(A/F)_5$ band of CH_4 -*para* H_2O . See the caption of Table XIV for more information.

$J', K' \leftarrow J'', K''$	Obs[MHz]	Obs	E' (sym)	E'' (sym)	Cal1	Cal2	$\langle\mu\rangle$	Obs - Cal1
Expt. (Ref. 1): Table VIII, $(A/F)_5$, $\Pi \leftarrow \Sigma$ band								
$1, 1 \leftarrow 2, 0$	827031.4	27.5868	$30.6874(F_1^+)$	$5.6100(F_2^+)$	25.0774	25.0	0.336	2.5094
$1, 1 \leftarrow 1, 0$	844268.9	28.1618	$30.6880(F_2^+)$	$5.0467(F_1^+)$	25.6413	25.5	0.607	2.5205
$2, 1 \leftarrow 2, 0$	844500.0	28.1695	$31.2579(F_1^+)$	$5.6100(F_2^+)$	25.6479	25.5	0.782	2.5216
$1, 1 \leftarrow 0, 0$	852462.1	28.4351	$30.6874(F_1^+)$	$4.7651(F_2^+)$	25.9223	25.8	0.505	2.5128
$2, 1 \leftarrow 1, 0$	860602.5	28.7066	$31.2559(F_2^+)$	$5.0467(F_1^+)$	26.2092	26.1	0.630	2.4974
$(A/F)_{5X}$, $\Pi \leftarrow \Sigma$ band (new)								
$1, 1 \leftarrow 2, 0$			$40.4223(F_1^+)$	$5.6100(F_2^+)$	34.8123		0.244	
$2, 1 \leftarrow 2, 0$			$40.9778(F_1^+)$	$5.6100(F_2^+)$	35.3678		0.521	
$1, 1 \leftarrow 1, 0$			$40.4237(F_2^+)$	$5.0467(F_1^+)$	35.3770		0.405	
$1, 1 \leftarrow 0, 0$			$40.4223(F_1^+)$	$4.7651(F_2^+)$	35.6572		0.324	
$2, 1 \leftarrow 1, 0$			$40.9734(F_2^+)$	$5.0467(F_1^+)$	35.9267		0.387	

TABLE XX: $(A/F)_6$ and $(A/F)_7$ band of $\text{CH}_4\text{-paraH}_2\text{O}$. See the caption of Table XIV for more information.

$J', K' \leftarrow J'', K''$	Obs[MHz]	Obs	E' (sym)	E'' (sym)	Cal1	Cal2	$\langle\mu\rangle$	Obs - Cal1
Expt. (Ref. 1): Table IX, $(A/F)_6$, $\Sigma \leftarrow \Pi$ band								
$1, 1 \leftarrow 2, 1$	889393.8	29.6670	$36.6994(F_1^+)$	$8.4919(F_2^+)$	28.2075	28.1	0.514	1.4595
$0, 1 \leftarrow 1, 1$	NA		$36.4139(F_2^+)$	$7.9119(F_1^+)$	28.5020		0.424	
$2, 1 \leftarrow 2, 1$	906302.4	30.2310	$37.2702(F_1^+)$	$8.5030(F_2^+)$	28.7672	28.6	0.666	1.4638
$1, 1 \leftarrow 1, 1$	906722.4	30.2450	$36.6994(F_1^+)$	$7.9157(F_2^+)$	28.7837	28.7	0.524	1.4613
$2, 1 \leftarrow 1, 1$	924003.8	30.8214	$37.2702(F_2^+)$	$7.9119(F_1^+)$	29.3583	29.2	0.321	1.4631
$(A/F)_{6X}$, $\Pi \leftarrow \Sigma$ band (new)								
$1, 0 \leftarrow 2, 1$			$29.3052(F_1^+)$	$8.5030(F_2^+)$	20.8022		0.349	
$0, 0 \leftarrow 1, 1$			$29.0337(F_1^+)$	$7.9157(F_2^+)$	21.1180		0.282	
$2, 0 \leftarrow 2, 1$			$29.8482(F_2^+)$	$8.4919(F_1^+)$	21.3563		0.439	
$1, 0 \leftarrow 1, 1$			$29.3052(F_1^+)$	$7.9119(F_2^+)$	21.3563		0.342	
$2, 0 \leftarrow 1, 1$			$29.8482(F_2^+)$	$7.9157(F_1^+)$	21.9325		0.193	
$(A/F)_{6Y}$, $\Pi \leftarrow \Sigma$ band (new)								
$1, 0 \leftarrow 2, 1$			$41.4654(F_1^+)$	$8.5030(F_2^+)$	32.9624		0.383	
$0, 0 \leftarrow 1, 1$			$41.1857(F_1^+)$	$7.9157(F_2^+)$	33.2700		0.317	
$2, 0 \leftarrow 2, 1$			$42.0249(F_2^+)$	$8.4919(F_1^+)$	33.5330		0.511	
$1, 0 \leftarrow 1, 1$			$41.4654(F_1^+)$	$7.9119(F_2^+)$	33.5330		0.395	
$2, 0 \leftarrow 1, 1$			$42.0249(F_2^+)$	$7.9157(F_1^+)$	34.1092		0.234	
Expt. (Ref. 1): Table IX, $(A/F)_{7a}$, $\Delta \leftarrow \Pi$ band								
$2, 2 \leftarrow 2, 1$	912803.3	30.4478	$37.6451(F_2^+)$	$8.4919(F_1^+)$	29.1532	29.0	0.545	1.2946
$2, 2 \leftarrow 1, 1$	930130.4	31.0258	$37.6451(F_2^+)$	$7.9157(F_1^+)$	29.7294	29.6	0.730	1.2964
Expt. (Ref. 1): Table IX, $(A/F)_{7b}$, $\Delta \leftarrow \Pi$ band								
$2, 2 \leftarrow 2, 1$	912529.1	30.4387	$37.6451(F_1^+)$	$8.5030(F_2^+)$	29.1421	29.0	0.554	1.2966
$2, 2 \leftarrow 1, 1$	930230.6	31.0292	$37.6451(F_1^+)$	$7.9119(F_2^+)$	29.7332	29.6	0.726	1.2960

TABLE XXI: $(A/F)_8$, $(A/F)_{8X}$, $(A/F)_{8Y}$ bands of $\text{CH}_4\text{-}para\text{H}_2\text{O}$. See the caption of Table XIV for more information. $(A/F)_{8X}$ and $(A/F)_{8Y}$ are the only bands from GM to SM.

$J', K' \leftarrow J'', K''$	Obs[MHz]	Obs	E' (sym)	E'' (sym)	Cal1	Cal2	$\langle\mu\rangle$	Obs - Cal1
Expt. (Ref. 1): Table VIII, $(A/F)_8$, $\Pi \leftarrow \Sigma$ band								
$1, 1 \leftarrow 2, 0$	901595.6	30.0740	$29.5596(A_2^+)$	$0.8678(A_1^+)$	28.6918	28.6	0.422	1.3822
$1, 1 \leftarrow 1, 0$	919166.0	30.6601	$29.5655(A_1^+)$	$0.2893(A_2^+)$	29.2762	29.1	0.742	1.3839
$2, 1 \leftarrow 2, 0$	919232.4	30.6623	$30.1455(A_2^+)$	$0.8678(A_1^+)$	29.2777	29.1	0.958	1.3846
$1, 1 \leftarrow 0, 0$	927673.3	30.9439	$29.5596(A_2^+)$	$0.0000(A_1^+)$	29.5596	29.4	0.610	1.3843
$2, 1 \leftarrow 1, 0$	936059.3	31.2236	$30.1280(A_1^+)$	$0.2893(A_2^+)$	29.8387	29.7	0.752	1.3849
$(A/F)_{8X}$, $\Sigma \leftarrow \Sigma$ band (new)								
$1, 0 \leftarrow 2, 0$			$34.6811(A_2^+)$	$0.8678(A_1^+)$	33.8133		0.310	
$0, 0 \leftarrow 1, 0$			$34.4127(A_1^+)$	$0.2893(A_2^+)$	34.1234		0.218	
$1, 0 \leftarrow 0, 0$			$34.6811(A_2^+)$	$0.0000(A_1^+)$	34.6811		0.214	
$2, 0 \leftarrow 1, 0$			$35.2176(A_1^+)$	$0.2893(A_2^+)$	34.9283		0.300	
$(A/F)_{8Y}$, $\Sigma \leftarrow \Sigma$ band (new)								
$1, 0 \leftarrow 2, 0$			$48.9812(A_2^+)$	$0.8678(A_1^+)$	48.1134		0.247	
$0, 0 \leftarrow 1, 0$			$48.7061(A_1^+)$	$0.2893(A_2^+)$	48.4168		0.171	
$1, 0 \leftarrow 0, 0$			$48.9812(A_2^+)$	$0.0000(A_1^+)$	48.9812		0.164	
$2, 0 \leftarrow 1, 0$			$49.5312(A_1^+)$	$0.2893(A_2^+)$	49.2419		0.227	

TABLE XXII: Microwave transitions of CH₄-H₂O. The band name and observed transitions are from Ref. 2. Lower levels in boldface are the lowest level of a particular symmetry. See the caption of Table XIV for more information.

Band[2]	$J', K' \leftarrow J'', K''$	Obs[MHz]	Obs	E' (sym)	E'' (sym)	Cal1	$\langle\mu\rangle$	Obs - Cal1
A^+, Σ	$1, 0 \leftarrow 0, 0$	8692.96	0.2900	$0.2893(A_2^+)$	0.0000 (A_1^+)	0.2893	0.199	0.0007
	$2, 0 \leftarrow 1, 0$	17383.05	0.5798	$0.8678(A_1^+)$	0.2893 (A_2^+)	0.5785	0.281	0.0013
F^-, Σ	$1, 0 \leftarrow 0, 0$	8504.65	0.2837	$11.5352(F_1^-)$	11.2533 (F_2^-)	0.2819	0.171	0.0017
	$2, 0 \leftarrow 1, 0$	17007.87	0.5673	$12.0991(F_2^-)$	11.5352 (F_1^-)	0.5639	0.242	0.0035
F^+, Σ	$1, 0 \leftarrow 0, 0$	8476.93	0.2828	$5.04673(F_1^+)$	4.7651 (F_2^+)	0.2816	0.234	0.0011
	$1, 0 \leftarrow 1, 0$	16953.03	0.5655	$5.61008(F_2^+)$	5.0467 (F_1^+)	0.5632	0.330	0.0023
A^-, Σ	$1, 0 \leftarrow 0, 0$	8690.39	0.2899	$7.28203(A_2^-)$	6.9932 (A_1^-)	0.2888	0.154	0.0011
	$2, 0 \leftarrow 1, 0$	17378.14	0.5797	$7.85948(A_1^-)$	7.2820 (A_2^-)	0.5774	0.219	0.0022
E^+, Π	$2, 1 \leftarrow 1, 1$	17120.06	0.5711	$13.6800(E^+)$	13.1100 (E^+)	0.5700	0.314	0.0011
E^-, Π	$2, 1 \leftarrow 1, 1$	17105.28	0.5706	$19.9619(E^-)$	19.3943 (E^-)	0.5676	0.228	0.0030
F^+, Π	$2, 1 \leftarrow 1, 1$	17421.68	0.5811	$8.49193(F_1^+)$	$7.9119 (F_2^+)$	0.5800	0.267	0.0012
	$2, 1 \leftarrow 1, 1$	17607.72	0.5873	$8.50303(F_2^+)$	$7.9157 (F_1^+)$	0.5873	0.267	0.0000
F^-, Π	$2, 1 \leftarrow 1, 1$	17396.81	0.5803	$15.1921(F_1^-)$	$14.6141 (F_2^-)$	0.5780	0.200	0.0023
	$2, 1 \leftarrow 1, 1$	17516.82	0.5843	$15.1993(F_2^-)$	$14.6165 (F_1^-)$	0.5828	0.200	0.0015

(a) $(A/F)_1$, $(A/F)_3$, and $(A/F)_{3X}$ bands

FIG. 1: Dore et al.'s $(A/F)_1$ and $(A/F)_3$ bands, shown in black arrows. Red levels and red arrows are new bands: $(A/F)_{1b}$ and $(A/F)_{3X}$. See Table XV for the corresponding transitions. To avoid clutter, only the $R(1)$ line from each band is shown, but $P(1)$, $P(2)$, $Q(1)$, $Q(2)$ and $R(0)$ lines are all observed.