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Calculation of Converged Rovibrational Energies and Partition Function for Methane using Vibrational-Rotational Configuration Interaction

Arindam Chakraborty, Donald G. Truhlar

Department of Chemistry and Supercomputing Institute, University of Minnesota, Minneapolis, MN 55455-0431

Joel M. Bowman, and Stuart Carter

Cherry L. Emerson Center of Scientific Computation and Department of Chemistry, Emory University, Atlanta, GA 30322

Abstract. The rovibration partition function of CH₄ was calculated in the temperature range of 100–1000 K using well-converged energy levels that were calculated by vibrational-rotational configuration interaction using the Watson Hamiltonian for total angular momenta $J = 0-50$ and the MULTIMODE computer program. The configuration state functions are products of ground-state occupied and virtual modals obtained using the vibrational self-consistent field (VSCF) method. The Gilbert and Jordan potential energy surface was used for the calculations. The resulting partition function was used to test the harmonic oscillator approximation and the separable-rotation approximation. The harmonic oscillator, rigid-rotator approximation is in error by a factor of two at 300 K, but we also propose a separable-rotation approximation that is accurate within 2% from 100 K to 1000 K.

I. INTRODUCTION

For accurate calculations of molecular energy levels, spectra, and thermochemistry, it is essential to take account of anharmonicity and the interaction between rotation and vibration. The coupling between rotation and vibration is due to Coriolis and centrifugal terms. A review of perturbation methods to account for anharmonicity and rotation-vibration coupling was given by Nielsen.¹ For a highly symmetric molecule like methane the anharmonicity and rotation-vibration interactions may be analyzed using group theory.^{2,3} Jahn used group theory and first order perturbation theory to treat rotation-vibration interactions in methane in a series of four papers.⁴⁻⁷ Later, second order and third order perturbation calculations were reported by Shaffer *et. al.*^{8,9} and by Hecht.^{10,11} More recently Lee *et. al.*¹² and Wang *et. al.*¹³ reported vibrational perturbation theory calculations on methane using an analytical potential energy surface.

Another approach to the computation of rovibrational levels of molecules is based on variational theory. The vibrational self-consistent field (VSCF) method¹⁴⁻¹⁹ is one such variational procedure. The VSCF procedure was extended by Carter *et. al.*^{20,21} to study rovibrational states by using the Whitehead-Handy^{22,23} implementation of the Watson²⁴ Hamiltonian. However, the VSCF method is not quantitatively accurate. A more accurate, systematically improvable procedure is vibrational-rotational configuration interaction²¹ (VRCI). The convergence of VRCI calculations can be accelerated by optimizing the basis functions using VSCF.¹⁸ A particularly efficient scheme, called virtual configuration interaction (VCI) is to use a ground-state VSCF calculation to generate single-mode functions and to use products of these single-mode functions (called modals) with rotational basis functions as basis functions with linear coefficients optimized by the variational principle.^{20,21} These functions are called configuration state functions (CSFs). In practice, as explained below, we actually used this procedure only for total angular momentum quantum number J equal to 0. For $J > 0$ the CSFs are constructed by taking the products of the $J = 0$ VCI eigenvectors with the rotational basis functions. A key advance²¹ in systematizing of the procedure is to organize the calculation using a hierarchical representation^{20,25} of the potential and limit the number of coupled modes in any included term to two, three, or four. Carter and

Bowman²⁶ used VCI with the hierarchical representation to calculate about a hundred vibrational levels for various isotopologs of CH₄ for $J = 0$ and 9 levels for CH₄ for $J = 1$.

Once the rovibrational energy levels are obtained by the VCI calculations for all important values of the angular momentum J , they can also be used to compute partition functions including full rotation-vibration coupling, but – prior to the present paper – this has not been done. In a $J = 0$ calculation, Bowman *et. al.*²⁷ showed that inclusion of anharmonic terms significantly lowers the zero-point energy of methane from its harmonic oscillator zero-point energy and increases the $J = 0$ partition function by a factor of 3.35–1.62 in the temperature range of 200–500 K; they also estimated rotational effects by using a calculation of the lowest-energy $J = 1$ states to estimate the rotational constant for a separable-rotation calculation.²⁷ Manthe *et. al.*²⁸ have also reported a $J = 0$ partition function for methane that was obtained using a different technique. The importance of anharmonicity for the vibrational energy of methane has also been shown in other recent work.^{29,30} The present paper includes fully converged vibrational states for J up to 50 in order to calculate a converged rotation-vibration partition function over the temperature range 100–1000 K. This is the first fully converged rotation-vibration partition function for any molecule with more than three atoms.

The potential energy surface used for the present calculations is that of Jordan and Gilbert,³¹ which is based on older work by Raff³² and Joseph *et. al.*³³ Although this is not a quantitatively accurate surface for methane, it is realistic enough for our purposes, and it has been used for recent rate constant calculations on the hydrogen atom^{27,34–50} and oxygen atom^{51,52} abstractions of a hydrogen atom from methane. Our goal is to obtain accurate rotation-vibration partition functions for a given realistic potential energy surface in order to assess the magnitude of the rotation-vibration coupling, and the well studied Jordan-Gilbert potential provides an ideal testing ground for this purpose.

Section II summarizes the theoretical formulation used in the present work, and Section III is devoted to the degeneracy and symmetry considerations. The eigenvalue calculations were carried out using a locally modified version of the MULTIMODE computer program,⁵³ and Section IV provides details of these calculations. Section V contains details of the partition function calculations. Section VI presents the results and discussion. The conclusions drawn from the present study are summarized in Sec. VII.

II. QUANTUM MECHANICAL THEORY

II.A. Application of the VSCF method for $J = 0$

The complete Watson Hamiltonian for a polyatomic molecule in normal coordinates is given by²⁰

$$H_{\text{Watson}} = -\frac{\hbar^2}{2} \sum_{k=1}^F \frac{\partial^2}{\partial Q_k^2} + \frac{\hbar^2}{2} \sum_{\alpha=1}^3 \sum_{\beta=1}^3 (J_\alpha - \pi_\alpha) \mu_{\alpha\beta} (J_\beta - \pi_\beta) - \frac{\hbar^2}{8} \sum_{\alpha=1}^3 \mu_{\alpha\alpha} + V(Q_1, \dots, Q_F), \quad (1)$$

where $(\alpha, \beta = x, y, z)$ and J_α and π_α are the components of the total and vibrational angular momentum operator respectively, μ is the effective reciprocal inertia tensor, Q_k is the mass-weighted normal coordinate⁵⁴ for mode k , and F is the number of vibrational degrees of freedom. The potential energy is a function of the normal coordinates and is given as $V(Q_1, \dots, Q_F)$. The first term in the above equation is the kinetic energy operator associated with each normal coordinate, the second term represents the coupling between the components of the angular momentum, and the third term, also known as the Watson term, is usually very small for polyatomic systems and is generally omitted from calculations. (However, it is included in the present work.)

For a non-rotating system, the VSCF method approximates the vibrational wave function as a Hartree product of single-mode wave functions called modals

$$\Psi(Q_1, \dots, Q_F) = \prod_{i=1}^F \phi_i(Q_i), \quad (2)$$

where $\phi_i(Q_i)$ is the modal associated with normal coordinate Q_i . The modals are constrained to be orthonormal:

$$\langle \phi_i | \phi_j \rangle = \delta_{ij}, \quad (3)$$

where δ_{ij} is the Kronecker delta. The VSCF method is a variational procedure for obtaining the modals, and the optimized wave function of the form in Eq. (2) is obtained by minimizing the total energy with respect to all the modals subject to the constraint of Eq. (3), which is enforced by the Lagrange multipliers. This variational procedure gives a set of differential equations for each modal

$$H_i^{\text{SCF}} \phi_i(Q_i) = \varepsilon_i \phi_i(Q_i), \quad (4)$$

for $i=1, \dots, F$, where ε_i is a Lagrange multiplier. Because H_i^{SCF} depends on the orbitals, this is not a conventional eigenvalue problem; it is called a pseudo-eigenvalue problem, and ε_i is the modal energy; these equations are solved iteratively. Using Eq. (1) with total angular momentum J equal to zero, the SCF Hamiltonian can be written as the following sum of kinetic and potential energy operators

$$H_i^{\text{SCF}} \equiv T_i + U_i, \quad (5)$$

where T_i is the kinetic energy operator associated with mode i , and is given as

$$T_i = -\frac{\hbar^2}{2} \frac{\partial^2}{\partial^2 Q_i}, \quad \text{for } i=1, \dots, F, \quad (6)$$

and U_i is known as the mean field operator and is given as

$$U_i = \left\langle \prod_{j \neq i}^F \phi_j(Q_j) \left| V(Q_1, \dots, Q_F) + \frac{\hbar^2}{2} \sum_{\alpha=1}^3 \sum_{\beta=1}^3 \pi_\alpha \mu_{\alpha\beta} \pi_\beta \right| \prod_{j \neq i}^F \phi_j(Q_j) \right\rangle. \quad (7)$$

In order to evaluate U_i , we have to perform an $(F-1)$ -dimensional integral over the normal coordinates, which is computationally intensive for most polyatomic systems. To make the calculations tractable, the potential energy term is expanded in a hierarchical fashion as²⁰

$$\begin{aligned} V(Q_1, \dots, Q_F) = & \sum_{i=1}^F V_i^{(1)}(Q_i) + \sum_{i=1}^F \sum_{j=1}^i V_{i,j}^{(2)}(Q_i, Q_j) + \sum_{i=1}^F \sum_{j=1}^i \sum_{k=1}^j V_{i,j,k}^{(3)}(Q_i, Q_j, Q_k) \\ & + \sum_{i=1}^F \sum_{j=1}^i \sum_{k=1}^j \sum_{l=1}^k V_{i,j,k,l}^{(4)}(Q_i, Q_j, Q_k, Q_l) + \dots \end{aligned} \quad (8)$$

By approximating the F -mode potential as a sum of one-mode, two-mode, three-mode, and four-mode terms, we have to evaluate only four-dimensional integrals. In principle, one should converge the expansion by including higher-order terms (five-mode, six-mode,...), but experience^{20,27} has shown that stopping at three-mode coupling is sometimes already well converged. In the present article, we will compare results obtained with three-mode coupling to those obtained with four-mode coupling.

The components of the vibrational angular momentum operator depend on two normal coordinates via the Coriolis coupling constant and are expressed as

$$\pi_\alpha = -i \sum_{k=1}^F \sum_{l=1}^F \zeta_{k,l}^\alpha Q_k \frac{\partial}{\partial Q_l}, \quad (9)$$

where $\zeta_{k,l}^\alpha$ is the Coriolis coupling constant.⁵⁵ The treatment of this term and the Watson term is explained elsewhere.²⁵

II.B. Configuration interaction

Since the modes are coupled, one needs to go beyond the VSCF approximation. The eigenfunctions of the ground-state SCF Hamiltonian for $J=0$ form an orthonormal basis, and the total vibrational wave function can be expanded in this basis; as mentioned in the introduction, this is called Virtual CI (VCI).^{20,21} For the calculations in this paper, we restrict the hierarchical expansion of Eq. (8) to at most four-mode coupling, and we form the VCI basis by one-mode, two-mode, three-mode, and four-mode excitations from the ground state. The one-mode excitations are limited by specifying the maximum number of quanta each mode can possess. Two-mode, three-mode, and four-mode excitations are limited by two parameters; one of them is the maximum number of quanta each mode can possess (called *maxbas*), and the other is the sum of quanta in all the modes (called *maxsum*). One could in principle use symmetry to block diagonalize the Hamiltonian,²⁶ but that was not done for the present calculations.

A general basis function for the VCI calculation is called a configurational state function (CSF) and is written as $|n_1 n_2 \dots n_i \dots n_F\rangle$, where F is the number of modes (9 for methane) and n_i is the number of quanta in mode i . All one-mode excitations of the form $|0_1 0_2 \dots n_i \dots 0_F\rangle$, are included, provided $n_i \leq \text{maxbas}(i, 1)$. All two-mode excited states of the form $|0_1 0_2 \dots n_i \dots n_j \dots 0_F\rangle$ are included, where the sum $n_i + n_j$ is less than or equal to $\text{maxsum}(2)$, and n_i and n_j are less than or equal to $\text{maxbas}(i, 2)$ and $\text{maxbas}(j, 2)$, respectively. Similarly, all three-mode and four-mode excitations of the form $|0_1 0_2 \dots n_i \dots n_j \dots n_k \dots 0_F\rangle$ and $|0_1 0_2 \dots n_i \dots n_j \dots n_k \dots n_l \dots 0_F\rangle$ are included, where $n_i + n_j + n_k$ is less than or equal to $\text{maxsum}(3)$, and $n_i + n_j + n_k + n_l$ is less than or

equal to $maxsum(4)$, respectively, and also where n_i is less than or equal to $maxbas(i, 3)$ for three-mode excitations and $maxbas(i, 4)$ for four-mode excitations.^{21,56}

II.C. Application of VCI method to $J > 0$

For the calculation of rotational-vibrational energy levels, the VCI scheme is applied with the full Watson Hamiltonian. The rovibrational basis in which the Watson Hamiltonian is diagonalized is obtained by taking the direct product between the VCI basis functions and symmetric-top wave functions.²⁰ The symmetric-top wave functions are labeled by three quantum number $|J, K, M\rangle$, where J is the angular momentum quantum number, K and M quantum numbers are associated with the projection of the angular momentum along the body-fixed z -axis, and the space-fixed Z -axis, respectively

$$\begin{aligned} J^2 |J, K, M\rangle &= J(J+1)\hbar^2 |J, K, M\rangle \\ J_z |J, K, M\rangle &= K\hbar |J, K, M\rangle \\ J_Z |J, K, M\rangle &= M\hbar |J, K, M\rangle \quad . \end{aligned} \quad (10)$$

All exact eigenvalues of the Watson Hamiltonian are independent of M so we consider only $M = 0$, and we write $|J, K, 0\rangle$ as $|J, K\rangle$. Equation (1) contains terms of the form $J_\alpha J_\beta$ where $\alpha, \beta = x, y, z$, and the matrix elements of these operators in the $|J, K\rangle$ basis can be obtained using raising and lowering operators. The non-zero matrix elements of all combinations of angular momentum operators occurring in Watson Hamiltonian have been given earlier by Bowman *et. al.*²⁰ and are shown in Appendix A. The matrix elements are non-zero only for $\Delta K = 0, \pm 1, \pm 2$. In the Watson Hamiltonian, each of these terms also involve an element $\mu_{\alpha\beta}$ of the inverse moment of inertia tensor, and the expressions in Eq. (1) that involve J_x, J_y, J_z also involve the vibrational angular momentum operators π_α . After all the matrix elements of the Hamiltonian are obtained, the Hamiltonian matrix is diagonalized in this rovibrational basis and the rotation-vibration energy levels are obtained.

III. SYMMETRY AND DEGENERACY OF ROTATION-VIBRATION STATES

Symmetry labeling of energy levels gives information about the degeneracies associated with the energy levels. In the present calculations, methane is treated as a molecule belonging to the C_1 point group. This gives us an opportunity to numerically verify the degeneracies associated with the vibrational and rovibrational energy levels of methane. Subsections A and B present a discussion on the symmetry of vibrational and rovibrational levels that is useful for analyzing the results. The inclusion of nuclear-spin degeneracy associated with rovibrational levels plays an important role in the computation of the partition function and is discussed Sec. III.C.

III.A. Vibrational symmetry

Methane belongs to the T_d point group and has nine vibrational degrees of freedom, which have only four unique frequencies. Of the nine vibrational modes, there is one non-degenerate mode with frequency ν_1 , one doubly degenerate mode with frequency ν_2 , and two triply degenerate modes with frequencies ν_3 and ν_4 . Note that, in keeping with the universally accepted language, we sometimes use the word “mode” to refer to the nine component modes, but elsewhere (as in the rest of this section) it refers to the four (possibly degenerate) modes. Rather than introducing a new notation when the above double usage is universally accepted we simply caution the reader about the context dependence of the word “mode.”

The four modes with unique frequencies ν_1, ν_2, ν_3 , and ν_4 can be labeled using the irreducible representation of the T_d point group, and the symmetry of the vibrational wave function can be obtained by taking a direct product of these four symmetry labels. The single degenerate mode with frequency ν_1 has symmetry A_1 , the doubly degenerate mode with frequency ν_2 has E symmetry, and each of the two triply degenerate modes have symmetry F_2 . The symmetries of the overtone states of the non-degenerate modes are obtained by taking a direct product of the symmetries of the fundamental states. When a mode is degenerate, the symmetries of its overtone states are not obtained simply by taking a direct product.⁵⁴ A detailed description on this topic is given elsewhere⁵⁴ along with a general expression for obtaining the symmetry of overtone states of

degenerate modes for any point group. The results of Herzberg^{57a} for the symmetry of overtone states of degenerate modes of methane are provided in the supporting information.⁵⁸ The symmetry of a combination state is obtained by simply taking the direct product of the individual mode symmetries. For example, a combination state in which there is one quantum each in ν_3 and ν_4 will have a symmetry of $A_1 + E + F_1 + F_2$ and can be obtained by taking a direct product of the F_2 irreducible representation with itself, but an overtone state with two quanta in ν_3 and zero quanta in ν_4 will span the $A_1 + E + F_2$ irreducible representations.

Finally, if a combination state arises due to multiple excitation of both degenerate and non-degenerate modes, the symmetry can be obtained by first evaluating the overtone symmetries of individual modes using the table in Ref. 57a or from the expression in Ref. 54 and then by taking the direct product of the symmetries associated with the combination. Note that in the case of methane, evaluating the direct product involving the symmetry of ν_1 is of no consequence since ν_1 has A_1 symmetry.

III.B. Rovibrational symmetry

The rotational wave function of any molecule can be labeled by the irreducible representations of the \mathcal{D}_∞^i group, which is the group of all rotations and reflections. The irreducible representations D_J^g are used to represent all rotational states with even J , and those of D_J^u are used to represent states with odd values of J . To label the rotational states of methane one has to reduce the representation of D_J^g and D_J^u to the irreducible representations of the T_d point group.⁷ The overall symmetry of the rovibrational wave function is obtained from the direct product of the symmetries associated with the vibrational and rotational wave functions in the T_d representation. Under the harmonic-oscillator rigid-rotator approximation, the degeneracy d associated with a generic rotation-vibration level of methane with n_i quanta in each ν_i and a total angular momentum of J is given as

$$d = \frac{(n_2 + 1)(n_3 + 1)(n_3 + 2)(n_4 + 1)(n_4 + 2)(2J + 1)^2}{4}. \quad (11)$$

Here we have used the fact that for a harmonic oscillator, a state with n quanta in a doubly degenerate mode is $(n+1)$ -fold degenerate, and a triply degenerate state with n quanta of excitation is $((n+1)(n+2)/2)$ -fold degenerate, and the spherical-top nature of methane gives the $(2J+1)^2$ degeneracy associated with the rotational wave function. The total degeneracy mentioned in Eq. (11) is preserved only for the idealized case of a rigid-rotator, harmonic oscillator Hamiltonian. The presence of anharmonic effects and rotation-vibration interactions lift some of the degeneracy. In addition, one must consider spin, as discussed in Subsection C.

The effect of Coriolis coupling on the vibrational levels of methane has been studied using group theoretic methods in a series of four papers by Jahn,⁴⁻⁷ and only the results of those studies that are needed for the present work are summarized here. It was shown by Jahn that the Coriolis coupling terms in the Watson Hamiltonian transform according to the F_1 irreducible representation of T_d point group.⁶ As a consequence, two vibrational states will be coupled by Coriolis interaction only when the direct product of their irreducible representations spans the F_1 irreducible representation.^{6,57b} Using the multiplication table⁵⁴ for the T_d point group, the irreducible representations spanned by $A_1 \times A_1$, $E \times E$, and $F_2 \times F_2$, are given as A_1 , $A_1 + A_2 + E$, and $A_1 + E + F_1 + F_2$, respectively. Since neither $A_1 \times A_1$ nor $E \times E$ spans F_1 , Coriolis splitting does not occur for non-degenerate and doubly degenerate modes of methane. It is only the two triply degenerate modes ν_3 and ν_4 of F_2 symmetry in which the three-fold degeneracy is lifted due to Coriolis coupling.

The interaction and the symmetry labeling of rovibrational levels of ν_3 and ν_4 are best studied using the irreducible representation of the full rotation-reflection group; hence our first task is to express the symmetry of triply degenerate modes using the irreducible representations of the full rotation-reflection group. It is shown in Ref. 7 and in the supporting information⁵⁸ that D_1^u is the irreducible representation for $J=1$ in the \mathcal{D}_∞^i group, and spans F_2 symmetry in the T_d point group. Since the two triply degenerate modes ν_3 and ν_4 span F_2 symmetry in T_d , one finds that ν_3 and ν_4 span D_1^u in the \mathcal{D}_∞^i group. To obtain the symmetries of the rovibrational levels, we have to obtain the

direct product between D_1^u and an irreducible representation of a rotational state. One of the advantages of working in the \mathcal{D}_∞^i group is the ease of evaluation of direct products between two irreducible representations. The direct product between two irreducible representations of \mathcal{D}_∞^i was discussed by both Wigner⁵⁹ and Hamermesh⁶⁰ and is summarized by:

$$D_{j_1} \times D_{j_2} = \sum_{J=|j_1-j_2|}^{|j_1+j_2|} D_J. \quad (12)$$

Using the above equation, the direct product between rotational states and the triply degenerate vibrational states is given as

$$\begin{aligned} D_1^u \times D_J^g &= D_{J-1}^u + D_J^g + D_{J+1}^u \quad (\text{even } J), \\ D_1^u \times D_J^u &= D_{J-1}^g + D_J^u + D_{J+1}^g \quad (\text{odd } J). \end{aligned} \quad (13)$$

The physical interpretation of this result is that the triply degenerate state has a vibrational angular momentum associated with it and the vibrational angular momentum interacts with the total angular momentum through the Coriolis coupling term; the vibrational angular momentum can be parallel, perpendicular, or antiparallel to the total angular momentum, which splits the levels. The levels resulting from the splitting of the triply degenerate state are labeled as F^+ , F^0 , and F^- , respectively.^{57b}

III.C. Nuclear spin degeneracy

The total wave function must be anti-symmetric with respect to exchange of both the coordinates and spins of identical fermions, and we must take account of this for the four identical protons in methane. As the Watson Hamiltonian does not include any nuclear spin, the only effect of inclusion of nuclear spin functions will be to increase the degeneracy associated with certain rovibrational levels. A system of m identical particles each with a nuclear spin of I has a total of $(2I + 1)^m$ spin states, and therefore, for methane the total number of possible spin states is 16. Because the total wave function must be anti-symmetric with respect to the exchange of any two hydrogen atoms in methane, not all of the 16-fold degeneracy is allowed for each rovibrational state. In order

to find the correct nuclear spin degeneracy associated with each rovibrational level, one has to evaluate a direct product between the permutation group symmetries of the rovibrational and nuclear spin states. The products that are totally symmetric, i.e., that belongs to the A_1 symmetry are the only combinations that exist in nature. The symmetry of the nuclear spin function for methane is $5A_1 + E + 3F_2$, and Wilson has reported⁶¹ a detailed description of the statistical weights associated with the rovibrational levels.

However, for statistical mechanical calculations at temperatures at which many rotational levels are occupied, one can replace the individual weights of the rovibrational state by an average weight to all states.^{61,62} The average weight is obtained by dividing the total nuclear spin multiplicity (16 for methane) by the symmetry number (12 for methane).

IV. EIGENVALUE CALCULATIONS

All the calculations were performed using the potential energy surface of Jordan and Gilbert,³¹ which was obtained from the POTLIB database.^{63,64} The rovibrational energy levels were calculated by the VCI method summarized in Sec. II; these calculations were carried out using a locally modified version of the MULTIMODE⁵³ program. The zero point energy of the system was taken as the zero of energy for all tabulated energy levels.

The first step of the calculation involves computation of the $J = 0$ VSCF Hamiltonian for the ground-state wave function. In this step the modals are expanded in harmonic oscillator functions; we used 12 harmonic oscillator functions in each mode. (A convergence check on this value is presented in Appendix B) The eigenvectors of the ground-state SCF Hamiltonian were used to perform the VCI calculations and the VCI matrix was constructed directly from the VSCF modals.

The number of basis functions used for this purpose were controlled by input parameters. As discussed in Sec. II.B, the VCI basis is formed by using a set of parameters called *maxsum* and *maxbas*. The maximum sum of quanta for one-mode, two-mode, three-mode, and four-mode coupling was fixed by giving appropriate values to *maxsum*(1), *maxsum*(2), *maxsum*(3), and *maxsum*(4). Then the maximum allowed quanta in mode i for one-mode, two-mode, three-mode, and four-mode excitations was fixed by

setting $maxbas(i,1)$, $maxbas(i,2)$, $maxbas(i,3)$, and $maxbas(i,4)$ equal to $maxsum(1)$, $maxsum(1) - 1$, $maxsum(1) - 2$, and $maxsum(1) - 3$, respectively. As an example, the procedure for obtaining the VCI basis for $J = 0$ is as follows. The maximum sum of quanta was taken to be 7 for one-mode, two-mode, and three-mode excitations, and 6 for four-mode excitations. The maximum allowed quanta in mode i for one-mode, two-mode, three-mode, and four-mode excitation was set to 7, 6, 5, and 4, respectively. The resulting size of the VCI matrix for $J = 0$ was 5650. In order to study the convergence we also performed calculations with smaller bases of sizes 715, 868, 1372, 1876, 2065, 2905, 4165, and 4390, and the corresponding $maxsum$ values are shown in Table I.

For $J > 0$, the Hamiltonian matrix was constructed by taking a direct product of the symmetric-top rotational functions²⁰ with the eigenfunctions of the $J = 0$ VCI matrix. If the N_{Vib} lowest-energy eigenfunctions are chosen, the size of the rovibrational matrix for angular momentum J is given by $N_{Vib}(2J + 1)$, and the rovibrational energies are obtained by diagonalizing a matrix of this order. The values used for N_{Vib} are specified in Sec. VI. Once the rovibrational basis is formed the matrix elements are computed using the equations in Appendix A. One can also use symmetry of the rovibrational basis function to expedite the process of forming the matrix, and a detailed description is presented in Ref. 20. However for the present calculations, methane was treated as a molecule of C_1 symmetry, and this allowed the degeneracies in energy levels associated with T_d point group can be verified numerically.

V. PARTITION FUNCTION CALCULATIONS

V.A. Accurate partition function

The canonical partition function was evaluated for a temperature range of 100 K to 1000 K by summing over all the rovibrational states as

$$Q(T) = \frac{(2I+1)^m}{\sigma} \sum_J (2J+1) \sum_{K=-J}^{+J} \sum_v \exp\left[\frac{-[E(v, J, K) + E^G]}{k_B T}\right], \quad (14)$$

where we have introduced a shorthand for the ground state energy

$$E^G \equiv E(0_1, \dots, 0_F, J = 0, K = 0), \quad (15)$$

and $I = \frac{1}{2}$, $m = 4$, σ is the symmetry number, the index ν denotes the collection of all the vibrational quantum numbers, and $E(\nu, J, K)$ is the $M = 0$ rovibrational energy that was obtained by the method discussed in Sec. II (details of the calculations are given in Sec. IV). The partition function in Eq. (14) can be expressed as

$$Q(T) = \tilde{Q}(T)e^{-E^G/k_B T}. \quad (16)$$

We note for reference that the converged value of E^G found in the present work is 9362 cm^{-1} . In the above equation, \tilde{Q} has the zero of energy at E^G , and Q has the zero of energy at the minimum value V_e of the potential energy. The vibrational partition function was calculated for the temperature range of 100–1000 K by summing over the computed vibrational states, and the sum over J in Eq. (14) was carried out through $J = 50$. The test for convergence with respect to J was done and the details are provided in the supporting information.⁵⁸ The partition functions calculated using the rovibrational levels obtained by solving the full Watson Hamiltonian were labeled as Q and \tilde{Q} without subscripts.

V.B. Approximations to be tested

Various sets of approximate partition functions were calculated using the separable-rotation approximation. Assuming separability of rotational and vibrational motion, the canonical partition function can be expressed as a product of vibrational (\tilde{Q}_{Vib}) and rotational (Q_{Rot}) partition functions

$$\tilde{Q}_{\text{SR}} = \tilde{Q}_{\text{Vib}}Q_{\text{Rot}}, \quad (17)$$

where the subscript ‘‘SR’’ is used to indicate that the partition function is calculated using the separable-rotation approximation. The vibrational partition function was calculated using two different methods. In the first method, \tilde{Q}_{Vib} was calculated from the harmonic frequencies obtained from normal mode analysis, and this harmonic oscillator vibrational partition function was labeled as $\tilde{Q}_{\text{Vib,HO}}$. The second method for obtaining \tilde{Q}_{Vib} used the vibrational energies obtained by solving the $J = 0$ Watson Hamiltonian for the given potential, and this anharmonic approximation was labeled as $\tilde{Q}_{\text{Vib},J=0}$.

The rotational partition function together with the nuclear spin contribution for any nonlinear molecule is given as

$$Q_{\text{Rot-Nuc}} = \frac{(2I+1)^m}{\sigma} \sum_J (2J+1) \sum_{K=-J}^{+J} \exp[-E_{\text{Rot}}(J,K)/k_B T], \quad (18)$$

where J is the angular momentum quantum number, and K is the projection of the angular momentum along a body-fixed z -axis. If we neglect centrifugal and Coriolis interactions, the rotational energy of a spherical top depends only on J :

$$E_{\text{Rot}} = BJ(J+1). \quad (19)$$

In Eq. (19), B is known as the spectroscopic rotational constant. Generally, B is evaluated from the principal moments of inertia at the equilibrium geometry, and then it is called B_e . In the present work, the rotational partition function was calculated using two methods. In the first case B_e was used for calculating the rotational energy by Eq. (19), and the nuclear-rotational partition function obtained from this method was labeled as $Q_{\text{Rot-Nuc,e}}$. In the second case, the Watson Hamiltonian was solved for each J value, and the rotational energies were obtained from the vibrational ground-state energies at each J . There are $(2J+1)$ vibrational ground state terms corresponding to $K = -J, \dots, +J$, and these were substituted in Eq. (18). The summation was carried out for $J = 1, \dots, 50$, and the computed nuclear-rotational partition function was labeled as $Q_{\text{Rot-Nuc,0}}$.

By combining the above treatments, four different separable-rotation partition functions were obtained and are summarized as follows:

$$\tilde{Q}_{\text{SR}}(W, G) = \tilde{Q}_{\text{Vib}, J=0} Q_{\text{Rot-Nuc,0}} \quad , \quad (20)$$

$$\tilde{Q}_{\text{SR}}(W, B_e) = \tilde{Q}_{\text{Vib}, J=0} Q_{\text{Rot-Nuc,e}} \quad , \quad (21)$$

$$\tilde{Q}_{\text{SR}}(\text{HO}, G) = \tilde{Q}_{\text{Vib, HO}} Q_{\text{Rot-Nuc,0}} \quad , \quad (22)$$

$$\tilde{Q}_{\text{SR}}(\text{HO}, B_e) = \tilde{Q}_{\text{Vib, HO}} Q_{\text{Rot-Nuc,e}} \quad , \quad (23)$$

where W denotes the use of the Watson Hamiltonian for $J = 0$, and G denotes the use of the ground vibrational state for each J .

For reference we note that the harmonic approximation to E^G yields 9530 cm^{-1} for the present potential energy surface. Using this value and Eqs. (16) and (20)–(23), we can also obtain four approximations to $Q(T)$, namely (W, G) , (W, B_e) , (HO, G) , and (HO, B_e) .

VI. RESULTS AND DISCUSSION

The zero point energy and the fundamental excitation energies for each of the four modes are shown in Table II. The average energies and the standard deviation (Δ) of some excited vibrational levels are shown in Table III. Note that under the harmonic oscillator approximation, each vibrational state discussed in Table III will be d -fold degenerate. (From this point on, we are discussing only $M = 0$ states. The full degeneracy is always $(2J + 1)$ times greater due to M degeneracy.) The value of d is

$d_0(2J + 1)$ where d_0 can be obtained by solving Eq. (11) with $J = 0$ for each vibrational level. However, the presence of anharmonic terms couples the normal modes resulting in partial loss of the d -fold degeneracy. A detailed description of the influence of anharmonicity on degenerate vibrational states of T_d molecules is given in Ref. 57c. It should be noted that lifting of the d -fold degeneracy is partial, and some states do not lose their degeneracy due to anharmonicity. Table III illustrates this for several vibrational states whose degeneracy is split by anharmonicity. The standard deviation Δ for each group of states considered in Table III was computed using the following expression

$$\Delta = \sqrt{\frac{\sum_i^d (E_i - \bar{E})^2}{d-1}}, \quad (24)$$

where E_i is the energy of the state i , and \bar{E} is the average energy, and d is the degeneracy in the absence of anharmonicity. Table III also shows the trend in the average energies and standard deviation with respect to the change in the VCI basis size. It is seen that increasing the basis has very little effect on the Δ values. It has been found that the average energy of states does not decrease monotonically with the VCI basis size. This is because on increasing the VCI basis size new energy levels are introduced which were missing in the smaller basis. Incorporation of new states changes the density of states associated with a given energy level. The density of states associated with the average

energies of 5650 VCI basis size is discussed in the supporting information.⁵⁸ It was also found that the density of states increases with increasing energy.

As discussed in Sec. III.B, no Coriolis splitting occurs for vibrational states of A_1 and E symmetries, and hence these states are expected to be $(2J + 1)$ and $2(2J + 1)$ fold degenerate, respectively, for any J , i.e., d_0 is 1 for A_1 states and 2 for E states. In Table IV, the values for the average energy of the vibrational ground state, singly excited ν_2 (E) state, and singly-excited ν_4 (F_2) state are listed for a few selected J values along with their respective standard deviation. The averages and the standard deviation at each J value for the states were computed over $(2J + 1)$, $2(2J + 1)$, and $3(2J + 1)$ values, respectively. The A_1 and E states showed a much smaller deviation from their respective mean values as compared to the F_2 state, indicating that three-fold degeneracy of the F_2 state was removed by Coriolis coupling. Since both A_1 and E states are strictly degenerate states, they should have zero standard deviation, but the results shown in Table IV have non-zero standard deviation due to the numerical methods used for computing them. This issue is discussed for the recent paper on H_3O^+ and D_3O^+ .⁶⁵

The effect of rotation-vibration coupling was also studied for various J values; the details of these studies are presented in both Appendix B and supporting information.⁵⁸ As discussed in Sec III.B, group theoretical methods provide us with the degeneracies associated with various rovibrational levels, and the numerical results were found to be in good agreement with the values predicted using group theory. The effect of using a 3-mode and a 4-mode representation on rovibrational energies was studied using $J = 20$ as an example. It was found that by increasing the representation from 3-mode to 4-mode, the minimum and the maximum rovibrational energies decreased by 2.5 and 5.7 cm^{-1} , respectively. This change corresponds to about 0.1% and is considered to be very small.

The expression for the partition function can be rewritten as

$$\tilde{Q}(T) = \sum_J \tilde{Q}_J(T) , \quad (25)$$

where \tilde{Q}_J is the contribution from each J level and is defined as

$$\tilde{Q}_J(T) = (2J + 1) \frac{(2I + 1)^m}{\sigma} \sum_{K=-J}^{+J} \sum_{\nu} \exp \left[\frac{-E(\nu, J, K)}{k_B T} \right]. \quad (26)$$

Since the computational effort to solve for the eigenvalues of the Watson Hamiltonian with a given J increases as J^2 , a compromise was achieved between computational effort and basis-set optimization effort by dividing the range of angular momentum under study into subsets and using a different value of N_{Vib} for each of them. The size of the rovibrational matrix is of the order of $N_{\text{Vib}}(2J + 1)$, and the diagonalization of the rovibrational matrix becomes computationally expensive for a high value of J and N_{Vib} . In order to keep the calculation tractable a converged value of N_{Vib} was obtained for the highest J value for each subset. For example, a converged value of N_{Vib} was obtained for $J = 10$ and was used for the set of J values in the range $5 < J < 10$. A similar procedure was used for $J = 15, 20$, and 25 , and converged values for \tilde{Q}_J were obtained. A list of N_{Vib} values used at different J states is provided in Table V, and the details of the convergence studies for these J states are summarized in Table VI, VII, and Appendix C. The convergence studies were carried out for the temperature range of 100–1000 K and converged values \tilde{Q}_J were obtained with respect to increasing the size of both the VCI and the rovibrational basis. For example, Table VI compares the \tilde{Q}_J values for $J = 10$ obtained from various VCI bases. It is seen that a VCI basis size of 5650 gives converged values over the entire temperature range. In these calculations, the rovibrational matrix was formed by using only the lowest N_{Vib} functions out of the full 5650 VCI functions. The N_{Vib} value is listed in Table V, and for $J = 10$, N_{Vib} was taken to be 500. The size of the rovibrational matrix formed is of order $N_{\text{Vib}}(2J + 1)$, and for $J = 10$ a rovibrational matrix of size 10500×10500 was diagonalized, and the rovibrational energies so obtained were used for calculating \tilde{Q}_J . Convergence with respect to N_{Vib} was checked by forming the rovibrational matrix using half the number of VCI functions. For $J = 10$, the value of N_{Vib} was reduced from 500 to 250 functions and the resulting size of the rovibrational matrix of 5250×5250 was obtained. As seen from Table VII, a rovibrational matrix that has only one quarter as many elements leads to a \tilde{Q}_J value that differ by less than 0.01% from the one computed with the larger basis. All the energy

levels that contributed more than or equal to 10^{-5} at 1000 K were include in the summation in Eq. (26). This corresponds to inclusion in the summation of all states that are below 8000 cm^{-1} .

Because of the importance of E^G for practical calculations, tests of its convergence are provided in the Appendix B, along with tests of the convergence of selected individual vibrational energy levels for $J = 10\text{--}25$.

The computed vibrational partition functions are shown in Table VIII. A converged value of $\tilde{Q}_{\text{Vib}, J=0}$ for 1000 K was obtained for a VCI matrix size of 4165. The vibrational partition function was computed using both 3-mode and 4-mode representations of the potential energy, and the results are given in Table IX; the 3-mode representation was found to be sufficiently accurate. In particular the differences of the 3-mode and the 4-mode results were less that 1%. Convergence with respect to the number of harmonic oscillator functions was verified, and vibrational partition functions obtained using 12 and 6 harmonic oscillator functions per modal were found to be within 0.1% of each other. A similar test was also performed for the Gauss-Hermite integration points, and the vibrational partition function obtained using 30 and 15 points were within 0.1% of each other.

The computed rovibrational partition function and the separable-rotation partition function are summarized in Table X. It was found that in the low-temperature region, the rigid-rotator harmonic oscillator $\tilde{Q}_{\text{SR}}(\text{HO}, B_e)$ partition function is very close to the accurate rovibrational partition function (\tilde{Q}), but the HO, B_e approximation begins to show significant errors as the temperature is increased, reaching 2% at 400 K and 9% at 1000 K. The separable-rotation partition function $\tilde{Q}_{\text{SR}}(\text{W}, \text{G})$, as described in Sec. IV, was found to agree closely with the accurate rotational-vibrational \tilde{Q} for all temperatures; thus this is an inexpensive alternative for computation of accurate rovibrational partition function. Because the method requires only the vibrational ground state energies for each of the $J > 0$ values, it does not require a large VCI and rovibrational basis.

The zero-point inclusive partition function is listed in Table XI, and it was found that the accurate rovibrational partition function is greater than the rigid-rotator harmonic oscillator partition function by a factor of 11.4 and 1.4 at 100 K and 1000 K, respectively. At 300 K the popular harmonic oscillator, rigid-rotator approximation underestimates the partition function Q by a factor of 2.3. Although \tilde{Q} is a more interesting quantity from the point of view of statistical mechanics (and is the quantity appearing in the textbooks), Q is the more interesting quantity from the point of view of practical applications because errors in calculating the zero point energy are equally as problematic as errors in calculating the thermal contributions. Again, the W,G approximation performs well. We should keep in mind, though, that CH₄ is probably close to a “best case scenario” for separable-rotation approximations in that the lack of any low-frequency modes greatly decreases the importance of rotation-vibration coupling. Now that we have demonstrated the feasibility of full thermodynamic rotation-vibration calculations for a pentatomic molecule, it will be interesting to test approximate theories for molecules with lower frequencies and large-amplitude motion.

VII. CONCLUSIONS

Fully converged rotational-vibrational partition functions of methane were computed by summing over the rovibrational levels for the temperature range of 100–1000 K, and the accurate results were compared with partition functions obtained using the separable-rotation approximation. The eigenvalues of the full Watson Hamiltonian were obtained using the computer program MULTIMODE and were converged with respect to VCI basis. The eigenvalues also showed the expected trends in degeneracy for a given J value. The difference in vibrational partition function for 3-mode and 4-mode expansion of the potential was found to be negligible for the present work.

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APPENDIX A

The angular momentum matrix elements needed for the VCI calculations are as follows:²⁰

$$\langle JK|J_z|JK\rangle = K \quad (\text{A1})$$

$$\langle JK|J_z^2|JK\rangle = K^2 \quad (\text{A2})$$

$$\begin{aligned} \langle JK|J_x^2|JK\rangle &= \langle JK|J_y^2|JK\rangle \\ &= \frac{1}{2}[J(J+1) - K^2] \end{aligned} \quad (\text{A3})$$

$$\begin{aligned} \langle JK \pm 1|J_x|JK\rangle &= \mp i \langle JK \pm 1|J_y|JK\rangle \\ &= \mp \frac{i}{2}[(J \mp K)(J \pm K + 1)]^{1/2} \end{aligned} \quad (\text{A4})$$

$$\begin{aligned} \langle JK \pm 2|J_x^2|JK\rangle &= -\langle JK \pm 2|J_y^2|JK\rangle \\ &= -\frac{1}{4}[(J \pm K + 1)(J \pm K + 2)(J \mp K)(J \mp K - 1)]^{1/2} \end{aligned} \quad (\text{A5})$$

$$\begin{aligned} \langle JK|J_x J_y|JK\rangle &= -\langle JK|J_y J_x|JK\rangle \\ &= -(iK/2) \end{aligned} \quad (\text{A6})$$

$$\begin{aligned} \langle JK \pm 1|J_z J_x|JK\rangle &= \mp i \langle JK \pm 1|J_z J_y|JK\rangle \\ &= (K \pm 1) \langle JK \pm 1|J_x|JK\rangle \end{aligned} \quad (\text{A7})$$

$$\begin{aligned} \langle JK \pm 1|J_x J_z|JK\rangle &= \mp i \langle JK \pm 1|J_y J_z|JK\rangle \\ &= K \langle JK \pm 1|J_x|JK\rangle \end{aligned} \quad (\text{A8})$$

$$\begin{aligned} \langle JK \pm 2|J_x J_y|JK\rangle &= \langle JK \pm 2|J_y J_x|JK\rangle \\ &= \mp \frac{i}{4}[(J \mp K - 1)(J \pm K + 2)(J \mp K)(J \pm K + 1)]^{1/2} \end{aligned} \quad (\text{A9})$$

Notice that we have corrected two typos in Ref. 20.

APPENDIX B

Table B-I provides the details of the convergence rate of the ground-state energy E^G using different VCI bases. The table also compares the E^G values obtained using 3-mode and 4-mode representations of the potential energy term. The ground-state energy obtained using different harmonic oscillator functions for each mode is also listed. Comparisons of the convergence for levels with $J > 0$ are more cumbersome because of the splitting associated with the $(2J + 1)$ values of the energy corresponding to different values of K for a given set of vibrational quantum numbers and a given total angular momentum J ; however it is interesting to compare the convergence of the lowest-energy and highest-energy K state, and this is done in Table B-II for $J = 10$. Similar comparison for higher values of $J = 15, 20$, and 25 is provided in the supporting information.⁵⁸

Table B-III and B-IV list the rovibrational states associated with the 0001 vibrational state for $J=1$ and 20, respectively. The 0001 vibrational state is three-fold degenerate and belongs to the F_2 irreducible representation of the T_d point group. (As in main text, we discuss only $M = 0$ states; there is an additional degeneracy of a factor $(2J + 1)$ due to M states, but this factor is not included in the present discussion.) The number rovibrational state associated with the 0001 vibrational state for any value of J is given by $3(2J + 1)$. Using this relation, the total number of rovibrational states for $J = 1$ and 20 are 9 and 123, respectively.

As discussed in Sec. III.B and Eq. (13), the rovibrational states can be labeled using the irreducible representations of the \mathcal{D}_∞^i symmetry group. The F_2 state of T_d point group transforms according to the D_1^u irreducible representation of the \mathcal{D}_∞^i group. The rovibrational states associated with any J value are given as

$$D_1^u \times D_J^g = D_{J-1}^u + D_J^g + D_{J+1}^u \text{ (even } J) \text{ ,} \quad (\text{B1})$$

$$D_1^u \times D_J^u = D_{J-1}^g + D_J^u + D_{J+1}^g \text{ (odd } J) \text{ .} \quad (\text{B2})$$

For $J=1$ and 20, the rovibrational states are given as,

$$D_1^u \times D_1^u = D_0^g + D_1^u + D_2^g \text{ ,} \quad (\text{B3})$$

$$D_1^u \times D_{20}^g = D_{19}^u + D_{20}^g + D_{21}^u \text{ .} \quad (\text{B4})$$

The rovibrational levels associated with each irreducible representation are given by $(2J+1)$ states. For $J=1$ case, the D_0^g , D_1^u , and D_2^g representations contribute 1, 3, and 5 states, respectively. For $J=20$, the D_{19}^u , D_{20}^g , and D_{21}^u representations contribute 39, 41, and 43 states, respectively, towards the total of 123 states. The representations can then be expressed in terms of the irreducible representation of the T_d point using the following relations⁶¹

$$D_0^g = A_1 \text{ ,} \quad (\text{B5})$$

$$D_1^u = F_2 \quad (\text{B6})$$

$$D_2^g = E + F_2 \quad (\text{B7})$$

$$D_{19}^u = 3A_1 + 3E + 10F_2 \quad (\text{B8})$$

$$D_{20}^g = 3A_1 + 4E + 10F_2 \quad (\text{B9})$$

$$D_{21}^u = 4A_1 + 3E + 11F_2 \text{ .} \quad (\text{B10})$$

The rovibrational levels associated with the 0001 vibrational state with $J=1$ are presented in Table B-III. The rovibrational states are symmetry labeled as $A_1 + E + 2F_2$ and exhibit the degeneracies associated with each symmetry label. For $J=20$, the number of

states arising from the D_{19}^u , D_{20}^g , and D_{21}^u representations are 39, 41, and 43, respectively, and are listed in Tables B-IV. It was found that the difference in energies of any two states belonging to different irreducible representation was very high as compared to the energy difference between consecutive states belonging to same irreducible representations. Because of the small energy difference between consecutive states it was not possible to assign T_d symmetry labels to each of them, but the appreciable energy difference between the states belonging to D_{19}^u , D_{20}^g , and D_{21}^u allowed us to divide the 123 rovibrational states in groups of 39, 41 and 43 states as predicted from the group theoretical treatment. The rovibrational energies obtained using the 4-mode representations are also shown in Table B-IV, and it was found that for the given set of rovibrational energies the 3-mode and the 4-mode representations gave converged results.

APPENDIX C

This appendix shows convergence studies similar to Table VI and VII (discussed in Sec. VI) but for $J = 15, 20, \text{ and } 25$. These results are in Tables C-I to C-VI.

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Table I. Values of *maxsum* used for forming various sizes of VCI basis for $J = 0$.

<i>maxsum</i> (1,2,3,4)	VCI size
4 4 4 4	715
5 5 4 4	868
5 5 5 4	1372
5 5 5 5	1876
6 6 5 5	2065
6 6 6 5	2905
6 6 6 6	4165
7 7 6 6	4390
7 7 7 6	5650

Table II. Fundamental excitation energies for $J=0$.^{a,b}

$\nu_1\nu_2\nu_3\nu_4$	Energy (cm^{-1})		
1000 (A_1)	2771		
0100 (E)	1444	1444	
0010 (F_2)	2930	2933	2933
0001 (F_2)	1282	1282	1283

^aCalculations were performed using 3-mode representation with 15 Gauss-Hermite integration points and 12 harmonic oscillator functions per mode.

^bThe zero point energy is 9362 cm^{-1} .

Table III. Average energy (in cm^{-1}) and standard deviation^a of excited vibrational states for $J=0$ with different sizes of VCI basis.^b

$\nu_1\nu_2\nu_3\nu_4$	d^c	715	868	1372	1876	2065	2905	4165	4390	5650
0002	6	2595 ± 35	2587 ± 38	2570 ± 39	2558 ± 35	2555 ± 36	2554 ± 37	2553 ± 37	2553 ± 37	2552 ± 38
0101	6	2749 ± 7	2748 ± 7	2716 ± 6	2716 ± 6	2716 ± 6	2715 ± 6	2713 ± 6	2713 ± 6	2713 ± 6
0003	10	3880 ± 53	3874 ± 57	3865 ± 60	3862 ± 61	3853 ± 65	3836 ± 66	3822 ± 63	3820 ± 65	3816 ± 67
0102	12	4025 ± 30	4024 ± 30	4018 ± 32	4013 ± 33	4012 ± 33	4002 ± 35	3984 ± 36	3984 ± 36	3982 ± 37
0202	18	5496 ± 20	5490 ± 19	5469 ± 26	5452 ± 29	5451 ± 28	5444 ± 30	5433 ± 31	5435 ± 33	5430 ± 35
0012	18	5542 ± 38	5542 ± 43	5533 ± 42	5525 ± 45	5531 ± 40	5513 ± 51	5484 ± 51	5484 ± 52	5490 ± 47
0111	18	5694 ± 18	5689 ± 15	5681 ± 16	5675 ± 18	5676 ± 18	5675 ± 19	5643 ± 15	5643 ± 15	5642 ± 17
1111	18	8442 ± 26	8446 ± 24	8459 ± 25	8448 ± 19	8453 ± 31	8436 ± 50	8418 ± 33	8426 ± 30	8423 ± 30

^aCalculated using Eq. (24).

^bCalculations were performed using 3-mode representation with 15 Gauss-Hermite integration points and 12 harmonic oscillator functions per mode.

^cThis is the degeneracy that the level would have in the absence of anharmonicity; it is the value used in Eq. (24).

Table IV. Average energy (in cm^{-1}) and standard deviation^a of vibrational states for selected values of J .^b

$\nu_1\nu_2\nu_3\nu_4$	d_0^c	1	5	10	15	20	25	50
0000	1	10 ± 0	156 ± 0	572 ± 0	1248 ± 0	2182 ± 0	3376 ± 1	13183 ± 7
0100	2	1455 ± 0	1603 ± 2	2027 ± 7	2713 ± 14	3661 ± 23	4866 ± 39	-
0001	3	1294 ± 6	1436 ± 21	1844 ± 39	2564 ± 306	3455 ± 229	4721 ± 440	-
0002	6	2562 ± 36	2702 ± 45	3101 ± 64	3755 ± 91	4681 ± 129	5839 ± 148	-
0101	6	2723 ± 8	2868 ± 24	3278 ± 42	3948 ± 67	4864 ± 88	6055 ± 127	-
0003	10	3825 ± 65	3961 ± 72	4353 ± 90	4995 ± 117	5901 ± 154	7052 ± 173	-
0102	12	3992 ± 37	4134 ± 49	4534 ± 71	5183 ± 95	6108 ± 141	7257 ± 125	-

^aCalculated using Eq. (24).

^bCalculations were performed using 3-mode representation with 15 Gauss-Hermite integration points and 12 harmonic oscillator functions per mode.

^cThe d value used in Eq. (24) is $(2J + 1)d_0$.

Table V. N_{Vib} values used in the calculations.^a

J	N_{Vib}
1	2000
2	1500
3	1000
4	800
5,...,10	500
11,...,15	300
16,..., 20	200
21,..., 25	200
26,..., 30	200
31,..., 50	100

^aFor VCI basis of size 5650.

Table VI. Convergence of \tilde{Q}_J with respect to change in VCI basis size for $J=10$.^a

VCI size	100 K	200 K	300 K	400 K	500 K	600 K	700 K	800 K	900 K	1000 K
715	0.156	9.57	38.09	78.22	126.32	183.84	254.35	342.45	453.33	592.42
4165	0.157	9.60	38.18	78.39	126.68	184.66	256.15	346.03	459.87	603.54
4390	0.157	9.61	38.18	78.39	126.68	184.67	256.16	346.06	459.93	603.65
5650	0.157	9.61	38.18	78.40	126.70	184.69	256.21	346.11	459.88	603.20

^aCalculations were performed using 3-mode representation with 15 Gauss-Hermite integration points and 12 harmonic oscillator functions per mode.

Table VII. Convergence of \tilde{Q}_J with respect to the change in rovibrational basis for $J=10$.^a

N_{Vib}	100 K	200 K	300 K	400 K	500 K	600 K	700 K	800 K	900K	1000 K
250	0.157	9.60	38.18	78.39	126.68	184.66	256.15	346.01	459.68	602.85
500	0.157	9.61	38.18	78.40	126.70	184.69	256.21	346.11	459.88	603.20

^aCalculations were performed using 3-mode representation with 15 Gauss-Hermite integration points and 12 harmonic oscillator functions per mode.

Table VIII. Comparison of $\tilde{Q}_{\text{Vib},J=0}$ for different size of VCI basis.^a

VCI size	100 K	200 K	300 K	400 K	500 K	600 K	700 K	800 K	900 K	1000 K
715	1.000	1.000	1.008	1.042	1.113	1.230	1.398	1.624	1.918	2.292
868	1.000	1.000	1.008	1.042	1.113	1.231	1.399	1.636	1.922	2.299
1372	1.000	1.000	1.008	1.042	1.114	1.232	1.402	1.632	1.932	2.316
1876	1.000	1.000	1.008	1.042	1.115	1.233	1.405	1.636	1.940	2.329
2065	1.000	1.000	1.008	1.042	1.115	1.234	1.405	1.637	1.941	2.331
2905	1.000	1.000	1.008	1.042	1.115	1.234	1.405	1.638	1.941	2.336
4165	1.000	1.000	1.008	1.042	1.115	1.234	1.406	1.640	1.947	2.342
4390	1.000	1.000	1.008	1.042	1.115	1.234	1.406	1.640	1.947	2.343
5650	1.000	1.000	1.008	1.042	1.115	1.234	1.406	1.640	1.948	2.345

^aCalculations were performed using 3-mode representation with 15 Gauss-Hermite integration points and 12 harmonic oscillator functions per mode.

Table IX. Computed $\tilde{Q}_{\text{Vib},J=0}$ values for 3-mode and 4-mode representation, using a VCI basis size of 5650.

T (K)	3-mode ^a	4-mode ^b
100	1.000	1.000
200	1.000	1.000
300	1.008	1.008
400	1.042	1.042
500	1.115	1.115
600	1.234	1.234
700	1.406	1.405
800	1.640	1.639
900	1.957	1.945
1000	2.342	2.340

^aVibration partition function was calculated using 3-mode representation with 15 Gauss-Hermite integration points and 12 harmonic oscillator functions per mode.

^bVibration partition function was calculated using 4-mode representation with 15 Gauss-Hermite integration points and 12 harmonic oscillator functions per mode.

Table X. Comparison of accurate rovibration partition functions with separable-rotation partition functions using a VCI basis of size 5650.^a

T (K)	\tilde{Q}	$\tilde{Q}_{\text{SR}}(\text{W}, \text{G})$	$\tilde{Q}_{\text{SR}}(\text{W}, B_e)$	$\tilde{Q}_{\text{SR}}(\text{HO}, \text{G})$	$\tilde{Q}_{\text{SR}}(\text{HO}, B_e)$
100	117	117	116	117	116
200	329	329	325	329	325
250	461	461	457	461	457
298	603	603	597	602	596
300	609	608	601	607	600
400	968	967	956	959	948
500	1448	1444	1428	1420	1404
600	2109	2101	2076	2041	2017
700	3032	3016	2980	2893	2859
800	4321	4299	4245	4067	4017
900	6103	6076	6015	5684	5613
1000	8616	8587	8479	7907	7807

^aCalculations were performed using 3-mode representation with 15 Gauss-Hermite integration points and 12 harmonic oscillator functions per mode.

Table XI. Comparison of zero-point-inclusive rovibration partition functions with separable-rotation partition functions using a VCI basis of size 5650.^a

T (K)	Q	$Q_{\text{SR}} (W, G)$	$Q_{\text{SR}} (W, B_e)$	$Q_{\text{SR}} (\text{HO}, G)$	$Q_{\text{SR}} (\text{HO}, B_e)$
100	3.74×10^{-57}	3.74×10^{-57}	3.70×10^{-57}	3.31×10^{-58}	3.28×10^{-58}
200	1.86×10^{-27}	1.86×10^{-27}	1.84×10^{-27}	5.54×10^{-28}	5.47×10^{-28}
250	1.84×10^{-21}	1.84×10^{-21}	1.83×10^{-21}	6.99×10^{-22}	6.93×10^{-22}
298	1.42×10^{-17}	1.42×10^{-17}	1.40×10^{-17}	6.27×10^{-18}	6.20×10^{-18}
300	1.93×10^{-17}	1.93×10^{-17}	1.91×10^{-17}	8.59×10^{-18}	8.49×10^{-18}
400	2.30×10^{-12}	2.30×10^{-12}	2.27×10^{-12}	1.24×10^{-12}	1.23×10^{-12}
500	2.89×10^{-9}	2.89×10^{-9}	2.85×10^{-9}	1.75×10^{-9}	1.73×10^{-9}
600	3.76×10^{-7}	3.74×10^{-7}	3.70×10^{-7}	2.43×10^{-7}	2.40×10^{-7}
700	1.33×10^{-5}	1.33×10^{-5}	1.31×10^{-5}	9.00×10^{-6}	8.90×10^{-6}
800	2.11×10^{-4}	2.10×10^{-4}	2.07×10^{-4}	1.46×10^{-4}	1.45×10^{-4}
900	1.93×10^{-3}	1.92×10^{-3}	1.90×10^{-3}	1.37×10^{-3}	1.36×10^{-3}
1000	1.22×10^{-2}	1.21×10^{-2}	1.20×10^{-2}	8.77×10^{-3}	8.66×10^{-3}

^aCalculations were performed using 3-mode representation with 15 Gauss-Hermite integration points and 12 harmonic oscillator functions per mode.

Table B-I. Convergence of ground-state energy (in cm^{-1}) with respect to size of VCI basis and number of modes coupled.

VCI size	Modes coupled	HO function per modal	E^G
715	3	12	9362.0013
868	3	12	9361.9295
1372	3	12	9361.8600
1876	3	12	9361.8506
2065	3	12	9361.7935
2905	3	12	9361.6712
4165	3	12	9361.5884
4390	3	12	9361.5833
5650	3	12	9361.5661
5650	4	12	9361.5652
5650	3	6	9361.5670

Table B-II. Comparison of the minimum and maximum rovibrational energy (in cm^{-1}) of selected vibrational states, computed using various VCI bases at $J = 10$.^a

$\nu_1\nu_2\nu_3\nu_4$	d_0 ^b	K ^c		715		4165		4390		5650	
		min	max	min	max	min	max	min	max	min	max
0000	1	-4	10	572	573	572	572	572	572	572	572
0100	2	-4	-3	2019	2037	2017	2035	2017	2035	2017	2035
0001	3	8	-1	1795	1898	1792	1894	1792	1894	1792	1894
0002	6	8	-5	3056	3264	3010	3221	3010	3221	3010	3221
0101	6	8	9	3259	3391	3222	3352	3222	3352	3222	3352
0003	10	8	9	4294	4598	4235	4551	4232	4550	4226	4548
0102	12	10	9	4477	4787	4435	4686	4435	4728	4433	4727

^aCalculations were performed using 3-mode representation with 15 Gauss-Hermite integration points and 12 harmonic oscillator functions per mode.

^bThe minimum and maximum energy levels were selected from 21 d_0 states (with $M = 0$) that have the indicated values of the four vibrational quantum numbers.

^cValues correspond to the VCI basis size of 5650.

Table B-III Rovibrational energies of 0001 vibrational state at $J = 1$.^a

$\nu_1\nu_2\nu_3\nu_4$	Energy (cm ⁻¹)		
0001 (A ₁)	1283.2		
0001 (F ₂)	1287.8	1287.9	1288.0
0001 (F ₂)	1296.9	1297.0	1297.1
0001 (E)	1297.3	1297.5	

^aCalculations were performed using 3-mode representation with 15 Gauss-Hermite integration points and 12 harmonic oscillator functions per mode.

Table B-IV Rovibrational energies (in cm^{-1}) of 0001 vibrational state at $J = 20$ for different irreducible representations^a with 3-mode and 4-mode coupling.^b

39 D_{19}^u states		41 D_{20}^g states		43 D_{21}^u states	
3-mode	4-mode	3-mode	4-mode	3-mode	4-mode
3334.7	3332.1	3395.4	3394.4	3474.5	3474.4
3334.7	3332.1	3395.4	3394.4	3474.6	3474.7
3335.5	3332.2	3395.5	3394.9	3475.5	3474.8
3335.5	3332.2	3395.5	3394.9	3475.5	3475.0
3335.6	3332.4	3395.6	3395.0	3475.6	3475.1
3335.6	3332.4	3395.6	3395.0	3475.9	3475.3
3335.8	3332.5	3410.8	3409.2	3476.1	3475.4
3335.8	3332.5	3410.8	3409.2	3476.4	3475.7
3336.1	3333.3	3411.0	3409.8	3493.1	3490.8
3336.1	3333.3	3411.1	3409.8	3493.2	3490.8
3336.6	3333.4	3411.2	3409.8	3493.3	3490.9
3336.6	3333.4	3411.2	3409.8	3493.9	3491.6
3336.7	3333.7	3422.4	3420.4	3494.3	3491.7
3336.9	3334.0	3422.4	3420.4	3496.2	3493.7
3337.1	3334.0	3422.9	3421.1	3496.3	3493.7
3337.4	3334.3	3422.9	3421.1	3496.4	3493.8
3337.4	3334.5	3423.0	3421.1	3499.1	3496.6
3337.5	3334.5	3423.0	3421.1	3499.4	3496.6
3337.6	3334.5	3431.8	3429.4	3499.5	3496.7
3338.0	3335.0	3431.8	3429.4	3503.9	3501.0
3338.1	3335.1	3432.4	3430.1	3504.1	3501.2
3338.9	3335.9	3432.5	3430.2	3504.2	3501.4
3338.9	3335.9	3432.7	3430.3	3504.3	3501.5
3339.1	3335.9	3432.7	3430.3	3504.8	3501.6
3339.1	3335.9	3438.8	3435.9	3505.1	3502.1

3339.6	3336.6	3439.3	3436.5	3512.5	3509.1
3339.6	3336.6	3440.0	3437.3	3512.5	3509.1
3341.4	3338.3	3440.2	3437.3	3512.7	3509.3
3341.4	3338.3	3440.5	3437.7	3512.7	3509.3
3341.6	3338.4	3440.6	3437.8	3513.2	3509.4
3341.6	3338.4	3444.0	3440.8	3513.2	3509.4
3342.0	3339.0	3444.1	3440.9	3523.0	3518.8
3342.0	3339.0	3444.6	3441.3	3523.0	3518.8
3345.5	3342.2	3448.1	3445.2	3523.2	3519.1
3345.5	3342.2	3448.2	3445.3	3523.2	3519.1
3345.7	3342.3	3448.2	3445.3	3523.7	3519.2
3345.7	3342.3	3449.4	3446.3	3523.7	3519.2
3345.9	3342.9	3450.1	3446.9	3535.9	3530.8
3345.9	3342.9	3450.5	3447.3	3535.9	3530.8
		3450.7	3447.3	3536.0	3531.0
		3450.9	3447.4	3536.0	3531.0
				3536.7	3531.1
				3536.7	3531.1

^aThe irreducible representations associated with $J = 20$ are D_{19}^u , D_{20}^g , and D_{21}^u , and were obtained using Eq. (B4).

^bCalculations were performed using 15 Gauss-Hermite integration points and 12 harmonic oscillator functions per mode.

Table C-I. Convergence of \tilde{Q}_J with respect to change in VCI basis size for $J=15$.^a

VCI size	100 K	200 K	300 K	400 K	500 K	600 K	700 K	800 K	900 K	1000 K
715	2.04×10^{-5}	0.162	3.25	15.02	39.49	79.55	138.84	222.44	336.94	490.03
4165	2.05×10^{-5}	0.162	3.26	15.06	39.61	79.92	139.85	224.80	341.73	498.76
4390	2.05×10^{-5}	0.162	3.26	15.06	39.61	79.92	139.85	224.82	341.77	498.85
5650	2.05×10^{-5}	0.162	3.26	15.06	39.61	79.93	139.89	224.92	342.08	499.65

^aCalculations were performed using 3-mode representation with 15 Gauss-Hermite integration points and 12 harmonic oscillator functions per mode.

Table C-II. Convergence of \tilde{Q}_J with respect to the change in rovibrational basis for $J=15$.^a

N_{Vib}	100 K	200 K	300 K	400 K	500 K	600 K	700 K	800 K	900 K	1000 K
200	2.05×10^{-5}	0.162	3.26	15.06	39.61	79.92	139.84	224.79	341.72	498.74
300	2.05×10^{-5}	0.162	3.26	15.06	39.61	79.93	139.89	224.92	342.08	499.65

^aCalculations were performed using 3-mode representation with 15 Gauss-Hermite integration points and 12 harmonic oscillator functions per mode.

Table C-III. Convergence of \tilde{Q}_J with respect to change in VCI basis size for $J = 20$.^a

VCI size	100 K	200 K	300 K	400 K	500 K	600 K	700 K	800 K	900 K	1000 K
715	5.32×10^{-11}	3.40×10^{-4}	6.43×10^{-2}	0.912	4.70	14.84	35.68	72.56	131.87	220.89
4165	5.17×10^{-11}	3.41×10^{-4}	6.45×10^{-2}	0.915	4.72	14.93	36.01	73.53	134.25	226.00
4390	5.17×10^{-11}	3.41×10^{-4}	6.45×10^{-2}	0.915	4.72	14.93	36.02	73.53	134.26	226.03
5650	5.18×10^{-11}	3.41×10^{-4}	6.45×10^{-2}	0.915	4.72	14.94	36.02	73.56	134.32	226.16

^aCalculations were performed using 3-mode representation with 15 Gauss-Hermite integration points and 12 harmonic oscillator functions per mode.

Table C-IV. Convergence of \tilde{Q}_J with respect to the change in rovibrational basis for $J = 20$.^a

N_{Vib}	100 K	200 K	300 K	400 K	500 K	600 K	700 K	800 K	900 K	1000 K
100	5.18×10^{-11}	3.41×10^{-4}	6.45×10^{-2}	0.915	4.72	14.93	36.01	73.53	134.25	226.00
200	5.18×10^{-11}	3.41×10^{-4}	6.45×10^{-2}	0.915	4.72	14.94	36.02	73.56	134.32	226.16

^aCalculations were performed using 3-mode representation with 15 Gauss-Hermite integration points and 12 harmonic oscillator functions per mode.

Table C-V. Convergence of \tilde{Q}_J with respect to change in VCI basis size for $J=25$

VCI size	100 K	200 K	300 K	400 K	500 K	600 K	700 K	800 K	900 K	1000 K
715	2.78×10^{-18}	9.83×10^{-8}	3.26×10^{-4}	1.93×10^{-2}	0.236	1.330	4.77	13.12	29.99	59.99
4165	2.80×10^{-18}	9.87×10^{-8}	3.27×10^{-4}	1.94×10^{-2}	0.237	1.329	4.82	13.34	30.69	61.83
4390	2.80×10^{-18}	9.87×10^{-8}	3.27×10^{-4}	1.94×10^{-2}	0.237	1.329	4.82	13.34	30.69	61.84
5650	2.80×10^{-18}	9.87×10^{-8}	3.27×10^{-4}	1.94×10^{-2}	0.237	1.330	4.83	13.34	30.70	61.86

^aCalculations were performed using 3-mode representation with 15 Gauss-Hermite integration points and 12 harmonic oscillator functions per mode.

Table C-VI. Convergence of \tilde{Q}_J with respect to the change in rovibrational basis for $J=25$

N_{Vib}	100 K	200 K	300 K	400 K	500 K	600 K	700 K	800 K	900 K	1000 K
100	2.80×10^{-18}	9.86×10^{-8}	3.26×10^{-4}	1.94×10^{-2}	0.236	1.33	4.83	13.34	30.70	61.86
200	2.80×10^{-18}	9.87×10^{-8}	3.27×10^{-4}	1.94×10^{-2}	0.237	1.33	4.83	13.34	30.70	61.86

^aCalculations were performed using 3-mode representation with 15 Gauss-Hermite integration points and 12 harmonic oscillator functions per mode.