

Complete nuclear motion Hamiltonian in the irreducible normal mode tensor operator formalism for the methane molecule

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A rovibrational model based on the normal-mode complete nuclear Hamiltonian is applied to methane using our recent potential energy surface [A. V. Nikitin, M. Rey, and V. G. Tyuterev, *Chem. Phys. Lett.* **501**, 179 (2011)]. The kinetic energy operator and the potential energy function are expanded in power series to which a new truncation-reduction technique is applied. The vibration-rotation Hamiltonian is transformed systematically to a full symmetrized form using irreducible tensor operators. Each term of the Hamiltonian expansion can be thus cast in the tensor form whatever the order of the development. This allows to take full advantage of the symmetry properties for doubly and triply degenerate vibrations and vibration-rotation states. We apply this model to variational computations of energy levels for $^{12}\text{CH}_4$, $^{13}\text{CH}_4$, and $^{12}\text{CD}_4$. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4730030>]

I. INTRODUCTION

An accurate computation and modeling of molecular rovibrational states of medium-sized molecules is still, even nowadays, an extremely challenging issue. In particular, the resolution of the complete nuclear Schrödinger equation for variationally fully converged energy levels up to highly excited vibrational states is very demanding. This is essentially due to high dimensionalities of the full vibration-rotation models including all degrees of freedom for the nuclear motion that require a development of efficient optimization methods as the number of atoms increases, especially when $N \geq 5$. Several authors have investigated the convergence for many hundreds or thousands of (ro)vibrational levels using various methods of global calculations and potential energy surfaces (PES) for small or medium-sized molecules.^{1–12} This implies using appropriately defined sets of coordinates to describe PESs and writing the kinetic energy terms to perform variational or perturbative calculations. In this vein, it has been recognized for many years that the sets of coordinates can be described either by curvilinear (bond-length, bond-angles, Jacobi, Radau, or hyperspherical)^{1,13–16} or rectilinear, normal coordinates.¹⁷ Each of them possess their advantages and disadvantages for practical applications. The exact Hamiltonian written in terms of rectilinear, normal coordinates has been derived by Wilson and Howard,¹⁸ Darling and Dennison,¹⁹ and simplified by Watson²⁰ that provides a rather general framework for describing rotation-vibration spectra of arbitrary N -atomic nonlinear semirigid molecular systems. There exists several computer programs (MULTIMODE, CONVIV, etc.) (Refs. 21–26) to solve the molecular stationary Schrödinger equation associated with this coordinate system. These codes are based on perturbation or variational theories using vibrational self-consistent field

(VSCF), mean field configuration interaction (VMFCI), or Lanczos methods. Alternative techniques use contact transformations (CT) in normal coordinates.^{27–29}

The curvilinear coordinates are usually considered as better suitable to describe the nuclear motions over a wide range of geometries but imply a treatment of complicated expressions of the kinetic energy operators as the number of atoms increases.^{14,30–35} There is a lot of works devoted to the calculation of vibrational energy levels using curvilinear internal coordinates.^{6,36–38} For systems with four or more atoms, Wang and Carrington used contracted basis functions combined with a Lanczos eigensolver for computing vibrational spectra.^{39,40} Among the most challenging issues the global and accurate modeling of the vibrational overtone energy levels of methane remains very important for various applications. Much progress has been achieved these last years in the construction of reliable PESs for CH_4 .^{37,41–44} Marquardt and Quack^{42,43} have computed a global PES for methane and have determined its analytical representation by adjustments to an *ab initio* data set under special consideration of additional experimental constraints. This PES has been applied to the calculations of vibrational levels in deuterated methane isotopologues.⁴³ Schwenke and Partridge^{37,44} have reported sophisticated *ab initio* calculations enabling accurate predictions of the lowest lying vibrational levels of CH_4 . Nikitin *et al.* have extended vibrational methane predictions using nonlinear internal coordinates from their PES, hereafter referred to as NRT PES.⁴⁵ In this work we focus on the development of irreducible tensor operator (ITO) formalism^{46,47,49,50} for the normal-mode vibrational-rotational Hamiltonian with a most complete account of symmetry properties for spherical top molecules (T_d , O_h point groups).

The detailed line-by-line analysis of high resolution experimental data of methane for excited vibrational polyads still remains a problem to be solved but is a requisite for numerous fields of science. For analyzing high-resolution

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spectra, the empirical effective polyad models proved to be efficient for the spectroscopic data reduction and gave rise to databases such as HITRAN,⁵¹ TDS,⁵² STDS,⁵³ etc., with applications to atmospheric physics or planetology (Giant planets or Titan atmospheres). Methane acts as a greenhouse gas in the earth atmosphere, knowledge of its absorption/emission is also important for astrophysical applications, in particular, for the modeling of brown dwarfs. Concerning the theoretical aspect, its high symmetry requires the use of sophisticated group theory tools and adapted computer codes. Mathematically speaking the ITO formalism allows a full account of molecular symmetry properties and is employed to describe—in a systematic way—anharmonicities as well as various vibration-rotation interactions as strong Fermi-type resonances between stretching and bending modes or Coriolis couplings. For this reason, advanced analyses of vibration-rotation spectra of spherical^{54–56,59} and symmetric-top^{60–64} molecules employ empirical models based on this approach for many years. However, these effective empirical models fail to describe reliably resonances for high polyads because of the lack of experimental informations for “dark states.”

Reliable predictions from molecular PESs would thus help resolving many issues related to the complete characterization of these unobserved dark states.

In this study, for the first time, the ITO normal-mode formalism is combined with molecular PESs for direct calculations of rovibrational methane states. The major aim of this work is to extend the empirical effective spectroscopic models to the complete normal-mode nuclear Hamiltonian using the ITO approach. To achieve this end, we generalize our previous work on symmetric top molecules⁶⁵ to systems where triply degenerate vibrational modes are involved. Convergence of basis set and of Hamiltonian expansion is discussed. The formalism is validated by calculations on methane isotopologues (¹²CH₄, ¹³CH₄, and ¹²CD₄) using NRT PES and comparisons with original variational calculations⁴⁵ in curvilinear internal coordinates.

II. QUANTUM MECHANICAL MODEL

A. Coordinate system

The choice of an optimal set of coordinates allowing the maximum separation of the individual motions in the molecule is of major importance for deriving quantum kinetic energy operators. To achieve this end, the space-fixed Cartesian coordinates $\mathbf{X}_i = (X_i, Y_i, Z_i)$ are transformed to describe internal motions of the molecule composed of N nuclei of mass m_i . First, a set of Cartesian coordinates $\mathbf{x}_i = (x_i, y_i, z_i)$ in the molecular fixed frame is defined as

$$\mathbf{X}_i - \mathbf{X}_{\text{cm}}^{(0)} = S^{-1}(\theta, \phi, \chi)\mathbf{x}_i, \quad (i = 1 \dots N), \quad (1)$$

where $\mathbf{X}_{\text{cm}}^{(0)}$ stand for the three coordinates of the center-of-mass, $S^{-1}(\theta, \phi, \chi)$ is an orthogonal 3×3 matrix relating the spatial orientation of the molecular fixed frame x, y, z to the laboratory-fixed frame X, Y, Z , and (θ, ϕ, χ) are the Euler angles. In the usual treatment of molecular vibrations it is customary to introduce $(3N - 6)$ internal displacement coordinates \mathbf{R}_i defined as components of the vector $\mathbf{R} = (r_1,$

$r_2, \dots; \theta_1, \theta_2, \dots)$ related to $(3N)$ Cartesian displacement \mathbf{d}_i . In general, the relation between \mathbf{R}_i and \mathbf{d}_i are nonlinear. By a linearization of these relations, one can define the rectilinear part $[\mathbf{R}]_{\text{rect}}$ of \mathbf{R} through the equation $[\mathbf{R}]_{\text{rect}} = \mathbf{B}_v \mathbf{d}$, where \mathbf{B}_v is a constant matrix.^{66–68} The 6 remaining equations are constrained according to the Eckart conditions⁶⁹ to preserve the same number of independent variables. Note that these conditions ensure that the molecular frame is properly locked with the molecule; the Eckart axes being chosen such that they coincide with the principle axes of inertia in the equilibrium configuration. For semirigid molecules with a well-defined equilibrium configuration the molecular vibrations are generally described by means of a set of $(3N - 6)$ nonredundant, rectilinear mass-weighted normal coordinates $Q_k \in (-\infty, +\infty)$ which are related to \mathbf{d}_i as^{17,66–68}

$$d_{i\alpha} = \sum_{k=1}^{3N-6} m_i^{-1/2} l_{i\alpha,k} Q_k \quad (\alpha = x, y, z; i = 1 \dots N). \quad (2)$$

For the XY₄ molecules ($N = 5$), we adopted the standard conventions about the orientation of the molecular fixed frame: at the equilibrium configuration the numbering of the atoms in the tetrahedron and their Cartesian coordinates $\mathbf{a}_i = (x_i, y_i, z_i)$ are defined as follows $Y(1) = (a, a, a)$, $Y(2) = (-a, -a, a)$, $Y(3) = (a, -a, -a)$, $Y(4) = (-a, -a, -a)$, $X(5) = (0, 0, 0)$ with $a = r_e/\sqrt{3}$.

The coordinate system is generally chosen to take full advantage of the symmetry. It is thus convenient to construct curvilinear symmetry-adapted coordinates $S_{k\sigma}^{(\Gamma)}$ with respect to the molecular point group as linear combination of the internal coordinates \mathbf{R}_i . We denote by \mathbf{U} the group symmetry transformation and we thus write

$$\mathbf{S}^{(\Gamma)} = \mathbf{U}\mathbf{R}. \quad (3)$$

Methane-type XY₄ molecules belong to the T_d point group and possess nine vibrational degrees of freedom divided into four modes. There is one non-degenerate mode (ν_1), one doubly degenerate mode (ν_2), and two triply degenerate modes (ν_3, ν_4) labeled using the irreducible representations (irreps) Γ of T_d , namely, A_1, E , and F_2 , respectively. Consequently the normal coordinates Q also transform according to the irreps of T_d and in the rectilinear approximation are related to the symmetry coordinates as

$$[\mathbf{S}^{(\Gamma)}]_{\text{rect}} = \mathbf{L}\mathbf{Q}^{(\Gamma)}, \quad (4)$$

with $\Gamma = A_1, E$, and F_2 . Here \mathbf{L} is the matrix composed of the eigenvectors of the $\mathbf{G}\mathbf{F}$ matrix in the conventional approach introduced by Wilson *et al.*¹⁷ In vibrational spectroscopy, it is often convenient to write the Hamiltonian in wavenumber units by introducing the harmonic frequencies ω_k and by replacing the normal coordinates $Q_{k\sigma}^{(\Gamma)}$ by their dimensionless equivalents $q_{k\sigma}^{(\Gamma)}$

$$\omega_{k\sigma} = \frac{1}{2\pi c} (\lambda_{k\sigma}^{(\Gamma)})^{1/2}, \quad q_{k\sigma}^{(\Gamma)} = \left(\frac{\lambda_k^{(\Gamma)}}{\hbar^2} \right)^{1/4} Q_{k\sigma}^{(\Gamma)}, \quad (5)$$

where $\lambda_{k\sigma}^{(\Gamma)}$ are the eigenvalues of the $\mathbf{G}\mathbf{F}$ matrix.¹⁷ Since the harmonic frequencies $(\omega_{2a}, \omega_{2b}), (\omega_{3x}, \omega_{3y}, \omega_{3z}),$ and $(\omega_{4x},$

ω_{4y}, ω_{4z}) are associated with doubly and two triply degenerate vibrations they will be simply denoted by ω_2, ω_3 , and ω_4 .

The initial PES is expressed in terms of curvilinear internal coordinates adapted to the symmetry of the molecule. In this work, the symmetrized curvilinear internal coordinates are defined as a linear combination of the Morse-cosines-type functions in the following manner:

$$\begin{aligned} S_1^{(A_1)} &= (y_1 + y_2 + y_3 + y_4)/2, \\ S_{2a}^{(E)} &= (2C_{12} - C_{13} - C_{14} + 2C_{34} - C_{23} - C_{24})/\sqrt{12}, \\ S_{2b}^{(E)} &= (C_{13} - C_{14} + C_{24} - C_{23})/2, \\ S_{3x}^{(F_2)} &= (y_1 - y_2 + y_3 - y_4)/2, \\ S_{3y}^{(F_2)} &= (y_1 - y_2 - y_3 + y_4)/2, \\ S_{3z}^{(F_2)} &= (y_1 + y_2 - y_3 - y_4)/2, \\ S_{4x}^{(F_2)} &= (C_{24} - C_{13})\sqrt{2}, \\ S_{4y}^{(F_2)} &= (C_{23} - C_{14})\sqrt{2}, \\ S_{4z}^{(F_2)} &= (C_{34} - C_{12})\sqrt{2}, \end{aligned} \quad (6)$$

with $y_i = 1 - \exp[-1.9(r_i - r_e)]$ and $C_{ij} = \cos(\theta_{ij}) - \cos(\theta_e)$, where $\cos(\theta_e) = -1/3$. The equilibrium length r_e is set to the optimized value accounting for best *ab initio* estimations,⁴⁵ in case of methane $r_e = 1.08601 \text{ \AA}$.

An appropriate analytical representation for the PES has to be conveniently chosen to describe the nine degrees of freedom of the CH₄ molecule. The NRT PES was built as a combination of the symmetrized powers of the $\{S_1^{(A_1)}, S_{2\sigma}^{(E)}, S_{3\sigma'}^{(F_2)}, S_{4\sigma''}^{(F_2)}\}$ curvilinear coordinates (6) as

$$V(\mathbf{R}) = \sum_{\{\mathbf{p}\}} \mathbf{F}_{\mathbf{p}} \prod_{i\sigma} \left(S_{i\sigma}^{(\Gamma_i)} \right)^{p_{i\sigma}}, \quad (7)$$

where the indices σ, σ' , and σ'' stand for components of degenerate vibrations. This can be expressed through a tensorial coupling scheme according to the algorithm proposed in Ref. 50. The following tensorial form for the PES expansion⁴⁵ is used here:

$$\begin{aligned} V(\mathbf{R}) &= \sum_{\{\mathbf{r}\}} \mathbf{F}'_{\mathbf{r}} \left(([S_1^{(A_1)}]^{r_1} \otimes [S_2^{(E)}]^{r_2})^{(C)} \right. \\ &\quad \left. \otimes ([S_3^{(F_2)}]^{r_3} \otimes [S_4^{(F_2)}]^{r_4})^{(C)} \right)^{(A_1)}, \end{aligned} \quad (8)$$

where $\mathbf{p} = \{p_1, p_{2a}, p_{2b}, p_{3x}, p_{3y}, p_{3z}, p_{4x}, p_{4y}, p_{4z}\}$, $\mathbf{r} = \{r_1, r_2, r_3, r_4\}$, and the sets $\mathbf{F}_{\mathbf{p}}, \mathbf{F}'_{\mathbf{r}}$ are force constants. The component-by-component PES expansion (7) contains 1118 inter-related parameters F up to 8th order expansion while its tensor form (8) contains 330 parameters F' given in supplementary materials of Ref. 45. This clearly indicates the advantage of using the full symmetry properties. The set of curvilinear coordinates for XY₄-type molecules consists of four bond-lengths $r_i \equiv r_{X-Y_i}$ and six angles $\theta_{ij} \equiv \theta_{Y_i-X-Y_j} = \arccos(\frac{\vec{r}_i \cdot \vec{r}_j}{r_i r_j})$ describing the nine vibrational degrees of freedom. Thus there exists a redundancy between these coordinates due to the fact that not all the six valence angles are independent which results in a nonlinear redundancy relation $\Theta(\mathbf{R}) = 0$. The redundancy issues are discussed, for example, in Refs. 70–72.

In this study we use rectilinear normal coordinates q_i defined by Eqs. (2), (4), and (5). In order to express curvilinear coordinates (6) in terms of nonlinear functions of q_i , we employed the techniques described in our previous work for symmetric top molecules⁶⁵ easily adapted to our case. An alternative technique of internal-to-normal coordinates has been outlined in Ref. 67. Assuming nuclear motions confined to the neighborhood of the equilibrium configuration and following the well-established procedure of a PES expansion in terms of dimensionless normal coordinates, we can write (in wavenumber units)

$$\begin{aligned} \frac{U(q)}{hc} &= \frac{1}{2} \sum_{i\sigma} \omega_i q_{i\sigma}^{2(\Gamma)} + \frac{1}{6} \sum_{i\sigma j\sigma' k\sigma''} \phi_{ijk}^{\sigma\sigma'\sigma''} q_{i\sigma}^{(\Gamma)} q_{j\sigma'}^{(\Gamma')} q_{k\sigma''}^{(\Gamma'')} \\ &\quad + \dots \end{aligned} \quad (9)$$

By symmetry consideration the anharmonicity normal-mode parameters $\phi_{ij\dots k}$ do not vanish if $\Gamma(q_i) \times \Gamma(q_j) \times \dots \times \Gamma(q_k) \supset A_1$.

B. Rovibrational normal-mode Hamiltonian in the ITO formalism

The complete vibration-rotation Hamiltonian for a polyatomic molecule in normal coordinates was formulated in its most compact form by Watson.²⁰ In terms of dimensionless normal coordinates and in wavenumber units ($H \leftarrow H/hc$) it is given by

$$\begin{aligned} H &= \frac{1}{2} \sum_{k\sigma} \omega_k p_{k\sigma}^{2(\Gamma)} + \frac{1}{2} \sum_{\alpha\beta} (J_\alpha - \pi_\alpha) \mu_{\alpha\beta} (J_\beta - \pi_\beta) \\ &\quad + U(q) + U_W, \end{aligned} \quad (10)$$

where $\alpha = x, y, z$, $J_\alpha \leftarrow J_\alpha/\hbar$ and $\pi_\alpha \leftarrow \pi_\alpha/\hbar$ are dimensionless molecular frame components of the total and vibrational angular momentum, respectively, and μ is the reciprocal inertia tensor. $U(q)$ is the potential function (9) and $U_W = -1/8 \sum_\alpha \mu_{\alpha\alpha}$ is a small mass-dependent contribution introduced by Watson²⁰ which is a purely quantum mechanical term of kinetic origin. The parameters $\omega_k, \mu_{\alpha\beta}, \phi_{ijk}^{\sigma\sigma'\sigma''}$, etc. are all expressed in cm^{-1} . The first term of the Hamiltonian is the vibrational kinetic energy operator while the second term describes the rotational kinetic energy including vibration-rotation couplings. For semirigid molecules, $\mu_{\alpha\beta}$ can also be expanded in convergent Taylor series in normal coordinates using the matrix algorithm described by Watson.²⁰ For spherical top molecules, the principal equilibrium moments of inertia are equal and the reciprocal inertia tensor reads

$$\begin{aligned} \mu &= I_0^{-1} \left(I_3 + I_0^{-1} \sum_{i\sigma} A_{i\sigma} q_{i\sigma} \right)^{-2}, \\ I_0 &= 2 \sum_i m_i a_\alpha^i a_\alpha^i, \quad \alpha = x, y, z, \quad i = 1, \dots, N = 5, \end{aligned} \quad (11)$$

where the a_α^i 's are the Cartesian coordinates at the equilibrium configuration (see below Eq. (2)) and $A_{i\sigma}$ is given in Ref. 73. The equilibrium rotational constant B_e for XY₄ molecules in

TABLE I. Coriolis coupling parameters $\zeta_{k\sigma,l\sigma'}^\alpha$ for $^{12}\text{CH}_4$, $^{13}\text{CH}_4$, and $^{12}\text{CD}_4$ from the PES.⁴⁵

$\zeta_{k\sigma,l\sigma'}^\alpha$	$^{12}\text{CH}_4$	$^{13}\text{CH}_4$	$^{12}\text{CD}_4$
$\zeta_{2a,3x}^x = -\zeta_{2a,3y}^y$	-0.68911	-0.69266	-0.64504
$\zeta_{2a,4x}^x = -\zeta_{2a,4y}^y$	-0.52452	-0.51983	-0.57786
$\zeta_{2b,3x}^x = -\zeta_{2b,3y}^y$	-0.39786	-0.39991	-0.37242
$\zeta_{2b,4x}^x = -\zeta_{2b,4y}^y$	-0.30283	-0.30012	-0.33363
$\zeta_{2b,3z}^z$	0.79572	0.79981	0.74483
$\zeta_{2b,4z}^z$	0.60566	0.60024	0.66725
$\zeta_{3y,3z}^x = -\zeta_{3x,3z}^y = \zeta_{3x,3y}^z$	0.50236	0.40442	0.16784
$\zeta_{4y,4z}^x = -\zeta_{4x,4z}^y = \zeta_{4x,4y}^z$	0.44976	0.45956	0.33216
$\zeta_{ky,lz}^x = -\zeta_{kx,lz}^y = \zeta_{kx,ly}^z$	-0.72291	-0.72013	-0.74547
$k, l = 3, 4, k \neq l$			

wavenumber units takes the value

$$B_e (\equiv \mu_{\alpha\alpha}^e/2) = \frac{6.321611}{m_Y r_e^2}. \quad (12)$$

For example, we have $B_e = 5.318311 \text{ cm}^{-1}$ for $^{12}\text{CH}_4$ and $^{13}\text{CH}_4$ and $B_e = 2.661200 \text{ cm}^{-1}$ for $^{12}\text{CD}_4$ in the Born-Oppenheimer approximation using the equilibrium configuration of Ref. 45.

When considering highly symmetric molecules the use of group theoretical methods and irreducible tensor operators adapted to the symmetry of the molecule turns out inherently advantageous to (i) describe degenerate vibrations and (ii) allow a systematic expansion of all possible intra-polyad and inter-polyad coupling terms. The irreducible tensor operators automatically account for all symmetry induced relations between degenerate components of the conventional approach. As a simple illustration, let us consider the Cartesian components ($\alpha = x, y, z$) of the vibrational angular momentum in the molecular fixed frame

$$\pi_\alpha = \sum_{k\sigma l\sigma'} \zeta_{k\sigma,l\sigma'}^\alpha \left(\frac{\omega_l}{\omega_k} \right)^{1/2} q_{k\sigma}^{(\Gamma)} p_{l\sigma'}^{(\Gamma')}, \quad (13)$$

where the ζ 's are the Coriolis coupling constants of normal modes defined via the l matrix⁶⁷ of Eq. (2). The ζ values are given in Table I for methane isotopologues. The axial vector π transforms according to the $\mathcal{D}^{(1-)}$ irreps ($\tau = g$) of the full rotation group $O(3)$ isomorphic to $SO(3) \otimes C_l$ and spans F_1 symmetry in the T_d point group. Here $\tau = g, u$ stands for the parity index and labels the irreps of the inversion group C_l . All operators are thus conveniently symmetrized in the $O(3) \supset T_d$ group chain. Similarly the total angular momentum J also transforms according to the F_1 irreps of T_d , that is $J_\alpha \equiv J_\alpha^{(1_g, F_1)}$. Accordingly one can rewrite Eq. (13) in tensor notation in a more compact form—where summations over components are hidden in the tensor product—as

$$\pi_\alpha^{(F_1)} = \sum_{kl} \xi_{k,l}^\alpha \left(\frac{\omega_l}{\omega_k} \right)^{1/2} \left(q_k^{(\Gamma)} \otimes p_l^{(\Gamma')} \right)_\alpha^{(F_1)}, \quad (14)$$

the ξ 's being defined as tensor Coriolis coupling constants. For a given set $(\sigma, \sigma', \alpha)$ these latter ones are related to the

ζ 's according to the formula:

$$\xi_{k,l}^\alpha = \frac{\zeta_{k\sigma,l\sigma'}^\alpha}{\sqrt{3} F \begin{pmatrix} \Gamma & \Gamma' & F_1 \\ \sigma & \sigma' & \alpha \end{pmatrix}}, \quad (15)$$

where the F 's are the Clebsh-Gordan (CG) coupling coefficients of T_d point group. The only non-vanishing $\zeta_{k\sigma,l\sigma'}^\alpha$ coefficients are those for which the selection rules of the CG coefficients are satisfied. For example the non-vanishing condition for the Coriolis terms $H_{\text{Cor}} = -2 \sum_\alpha B_e \pi_\alpha J_\alpha + \dots$ in Eq. (10) reads $\Gamma(q_k) \times \Gamma(p_l) \supset \Gamma(J_\alpha)$. We clearly see from Eq. (14) that the product of two modes must span the F_1 representation that implies that the ν_1 mode will not be coupled by Coriolis interactions with other modes. If the doubly degenerate mode is not involved, then the interactions terms and the symmetry labeling can be studied in the full rotation group according to the natural branching rule $\mathcal{D}^{(1_u)} \rightarrow F_2$ for the ν_3 and ν_4 modes. In that case, the Coriolis coupling terms evaluated at the equilibrium geometry can be cast into the following form:

$$H_{\text{Cor}} \sim 2\sqrt{3} B_e (\pi^{(1_g)} \otimes J^{(1_g)})^{(0_g, A_1)}, \quad (16)$$

where the three components ($m = 0, \pm 1$) of the first-rank π tensor are given by

$$\pi_m^{(1_g)} = \sum_{kl} \xi_{k,l}^{(m)} \left(\frac{\omega_l}{\omega_k} \right)^{1/2} \left(q_k^{(1_u)} \otimes p_l^{(1_u)} \right)_m^{(1_g)}. \quad (17)$$

By considering the appropriate orientation, we can relate them with Cartesian components

$$\begin{aligned} \pi_x^{(F_1)} &= -\frac{1}{\sqrt{2}} (\pi_1^{(1_g)} - \pi_{-1}^{(1_g)}), \\ \pi_y^{(F_1)} &= -\frac{i}{\sqrt{2}} (\pi_1^{(1_g)} + \pi_{-1}^{(1_g)}), \\ \pi_z^{(F_1)} &= \pi_0^{(1_g)}. \end{aligned} \quad (18)$$

Expanding these latter relations in both sides of equations and using Eqs. (14) and (17) we can deduce that

$$\xi_{k,l}^{(\pm 1)} = \pm i \xi_{k,l}^{(x)} = \mp i \xi_{k,l}^{(y)}, \quad \xi_{k,l}^{(0)} = -i \sqrt{2} \xi_{k,l}^{(z)}. \quad (19)$$

Note that in general case where all modes are involved, all the couplings are arranged in T_d point group. The reason is that there is no irrep of the $O(3)$ rotation group which subduces to an E type one. A way to overcome this will be the use of the $u(2)$ formalism which has been considered for twofold oscillators and doublet electronic states.⁷⁴

It is thus *a priori* possible to express individually by “hand” each term of the Hamiltonian in a tensor form which—nevertheless—remains a tedious and tricky task. This work aims at providing a systematic and unified procedure to derive the complete nuclear Hamiltonian (10) in terms of ITOs. To achieve this end and following Ref. 65 the first step will consist in transforming the normal-mode Hamiltonian using creation and annihilation operators. These latter ones appear to be more convenient to handle complicated algebraic expressions as well as to compute matrix elements. The selection rules are thus directly deduced from the second quantized form. This procedure has been already described elsewhere in

details for symmetric top molecules (see Ref. 65). We expand Eq. (10) as

$$H(a^+, a, J_\alpha) = \sum_{\text{all indices}} h_{\mathbf{m}, \mathbf{n}}^{n_\alpha, n_\beta} \varepsilon \mathcal{V}_{\mathbf{m}, \mathbf{n}} (J_\alpha)^{n_\alpha} (J_\beta)^{n_\beta}, \quad (20)$$

where the following vibrational representation is employed:

$$\begin{aligned} \varepsilon \mathcal{V}_{\mathbf{m}, \mathbf{n}} = & \frac{1}{2} \left(\prod_{k\sigma} (a_{k\sigma}^{+(\Gamma)})^{m_{k\sigma}} (a_{k\sigma}^{(\Gamma)})^{n_{k\sigma}} \right. \\ & \left. + \varepsilon \prod_{k\sigma} (a_{k\sigma}^{+(\Gamma)})^{n_{k\sigma}} (a_{k\sigma}^{(\Gamma)})^{m_{k\sigma}} \right). \end{aligned} \quad (21)$$

Here the ε index stands for hermiticity (+) or anti-hermiticity (−) and $n_\alpha + n_\beta \leq 2$. In order to fully take advantage of the molecular symmetry, we want to express the Hamiltonian (20) in a systematic way in terms of rotation-vibration ITO. As was argued in Ref. 65 in the case of symmetric tops, the choice of the formalism proposed by Nikitin *et al.*⁵⁰ is very relevant to systematically express the Hamiltonian at arbitrary order of the development. For the vibrational part, symmetrized powers of creation and annihilation operators are built with specific formulations adapted to non-degenerate, twofold or threefold vibrations. The symmetrized powers are obtained as

$$\mathcal{A}^{+(l, A_1)} = \mathcal{N} (a^{+(A_1)})^l \quad (A_1 \text{ modes}),$$

$$\mathcal{A}_\sigma^{+(lm, \Lambda)} = \mathcal{N} \sum_{\alpha} (lm) \mathcal{G}_{\alpha\sigma}^{\Lambda} b_1^{+l} b_2^{+m} \quad (E \text{ modes}),$$

$$\mathcal{A}_\sigma^{+(lmn, k\Lambda)} = \mathcal{N} \sum_{\alpha} (lmn) \mathcal{G}_{\alpha\sigma}^{k\Lambda} a_x^{+l} a_y^{+m} a_z^{+n} \quad (F_2 \text{ modes}), \quad (22)$$

where for E -type modes, the two linear combinations $b_1 = (a_1 + ia_2)/\sqrt{2}$ and $b_2 = (a_1 - ia_2)/\sqrt{2}$ are introduced. \mathcal{N} is a normalization factor, α stands for all rearrangements of (lmn) and \mathcal{G} is a unitary transformation⁵⁰ allowing the orientation into T_d . The multiplicity k index is used to distinguish tensors of the same irreducible representation Λ . The annihilation part is obtained in a similar manner and the creation-annihilation couplings are defined in the abbreviated notations as $\mathcal{L}_1^{(A_1)} = (\mathcal{A}^{+(l_1, A_1)} \otimes \mathcal{A}^{(l_1, A_1)})^{(A_1)}$ for the non-degenerate mode, $\mathcal{L}_{2\sigma_2}^{(\Gamma_2)} = (\mathcal{A}^{+(l_2 m_2, \Lambda_2)} \otimes \mathcal{A}^{(l_2 m_2, \Lambda_2)})_{\sigma_2}^{(\Gamma_2)}$ for the twofold degenerate mode and $\mathcal{L}_{i\sigma_i}^{(\Gamma_i)} = (\mathcal{A}^{+(l_i m_i n_i, k_i \Lambda_i)})_{\sigma_i}^{(\Gamma_i)} \otimes \mathcal{A}^{(l_i m_i n_i, k_i \Lambda_i)}_{\sigma_i}^{(\Gamma_i)}$ ($i = 3, 4$) for the threefold degenerate modes. Thus, the resulting four-mode coupling for methane-type XY_4 molecules is given by

$$\begin{aligned} V_{\{\mathbf{l}'\mathbf{m}'\mathbf{n}'\}\{\mathbf{l}\mathbf{m}\mathbf{n}\}\sigma_v}^{(\mathbf{k}'\Lambda', \mathbf{k}\Lambda)\Gamma_2\Gamma_3\Gamma_4\Gamma_{34}(\Gamma_v)} = & ((\mathcal{L}_1^{(A_1)} \otimes \mathcal{L}_2^{(\Gamma_2)})^{(\Gamma_2)} \\ & \otimes (\mathcal{L}_3^{(\Gamma_3)} \otimes \mathcal{L}_4^{(\Gamma_4)})^{(\Gamma_{34})})_{\sigma_v}^{(\Gamma_v)}, \end{aligned} \quad (23)$$

where $\{\mathbf{l}\mathbf{m}\mathbf{n}\} \setminus (\mathbf{k}\Lambda) = (l_1)(l_2 m_2)(l_3 m_3 n_3)(l_4 m_4 n_4) \setminus (A_1)(\Lambda_2)(k_3 \Lambda_3)(k_4 \Lambda_4)$. The degrees in creation (respectively, annihilation) operators for each mode are given by $N'_i = l'_i + m'_i + n'_i$ (respectively, $N_i = l_i + m_i + n_i$) and characterize the vibrational operators. For the sake of simplicity, the set $(l_i m_i n_i)$ will be omitted if N_i are equal to zero and denoted as $(lmn)_i$ otherwise. Only labels which are different from zero inside a subset are kept in the simplified notation. Following this, we write, for example, the set $\{\mathbf{l}\mathbf{m}\mathbf{n}\} = (0)(00)(100)(210)$

simply as $(1)_3(21)_4$. Similarly, we denote $(k'_i \Lambda'_i, k_i \Lambda_i)$ as $(k' \Lambda', k \Lambda)_i$ and we omit this factor if $N'_i = N_i = 0$. Though this tensorial form seems somewhat unwieldy a considerable simplification can be achieved since generally many N_i and N'_i are equal to zero.

Finally, omitting all intermediate indices, hermitian or anti-hermitian vibrational operators may be constructed in concise notations as

$$\varepsilon V_{\sigma_v}^{(\Gamma_v)} = e^{i\phi} V_{\sigma_v}^{(\Gamma_v)}, \quad (24)$$

for diagonal operators, that is when all $(N'_i, k'_i \Lambda'_i)$ and $(N_i, k_i \Lambda_i)$ labels are equal and

$$\varepsilon V_{\sigma_v}^{(\Gamma_v)} = e^{i\phi} (V_{\sigma_v}^{(\Gamma_v)} + \varepsilon (V_{\sigma_v}^{(\Gamma_v)})^+), \quad (25)$$

otherwise. Here ε denotes the parity of the operator. The phase factor $e^{i\phi}$ depends on the parity and is set to $e^{i\phi} = i$ for odd operators ($\varepsilon = -$) and to 1 otherwise ($\varepsilon = +$). We give in Table II the correspondences between tensor and component-by-component formulations for selected vibrational operators. In the simplified notations of Table II and in the examples which follow, the multiplicity indices are omitted as they appear only for higher order terms.

Concerning the rotational part, the operators $R_m^{\Omega(K)}$ of degree Ω in J_α and of rank K in $O(3)$ are built recursively from successive couplings of the elementary tensor $R^{1(1)} = 2\mathbf{J}$ following the method proposed by Moret-Bailly and Zhilinskii.^{75,76} Thus, symmetry-adapted tensor operators in $O(3) \supset T_d$ are obtained through a unitary transformation $R_\alpha^{\Omega(K, nC)} = \sum_m (K) G_{nC\alpha}^m R_m^{\Omega(K)}$, where the G matrix elements can be found in Ref. 78 and n a multiplicity index. The same transformation is used to construct symmetrized angular momentum functions. The Hamiltonian being hermitian and invariant under time-reversal, the operators V and R have necessarily the same parity in elementary operators that is $\varepsilon = (-1)^\Omega$ in (24). For our purposes the complete nuclear Hamiltonian is such that $\Omega \leq 2$ and the set of multiplicity free ($n = 1$) rotational operators involved in the complete nuclear Hamiltonian is given by

$$\begin{aligned} R^{2(0, A_1)} &= -\frac{4}{\sqrt{3}} (J_x^2 + J_y^2 + J_z^2), \\ R_\alpha^{1(1, F_1)} &= 2J_\alpha \quad (\alpha = x, y, z), \\ R_a^{2(2, E)} &= \frac{2\sqrt{2}}{\sqrt{3}} (2J_z^2 - J_x^2 - J_y^2), \\ R_b^{2(2, E)} &= 2\sqrt{2} (J_x^2 - J_y^2), \\ R_\alpha^{2(2, F_2)} &= 2\sqrt{2} (J_\beta J_\gamma + J_\gamma J_\beta), \end{aligned} \quad (26)$$

where (α, β, γ) are circular permutations with the commutation rules $[J_x, J_y] = -iJ_z$ in the molecular frame.²⁰ Having defined the vibrational and rotational parts, we can form rovibrational tensor operators which are totally symmetric in the molecular point group. The Hamiltonian is built in a systematic way as a linear combination of such tensors

$$H(a^+, a, J_\alpha) = \sum_{\text{all indices}} t_{\{\mathbf{l}\mathbf{m}\mathbf{n}\}}^{\Omega(K, \Gamma)} \beta (\varepsilon V^{(\Gamma)} \otimes R^{\Omega(K, \Gamma)})^{(A_1)}, \quad (27)$$

where β is a numerical factor initially introduced to set scalar terms equal in both tensorial and standard notations. This is essentially the same Hamiltonian as Eq. (20) but written

TABLE II. Explicit expressions for low-order ITO vibration operators.

ITO form	σ	Tensor components
$+V_{\{(2)_1\}\{(2)_1\}}^{A_1 A_1 A_1 A_1(A_1)}$		$\frac{1}{2}a_1^{+2}a_1^2$
$+V_{\{(1)_2\}\{(1)_2\}}^{(E,E)_2 A_1 A_1 A_1(A_1)}$		$\frac{1}{\sqrt{2}}\sum_{\sigma} a_{2\sigma}^+ a_{2\sigma}$
$+V_{\{(1)_i\}\{(1)_i\}}^{(F_2, F_2)_i A_1 A_1 A_1(A_1)}$		$\frac{1}{\sqrt{3}}\sum_{\sigma} a_{i\sigma}^+ a_{i\sigma} \quad (i = 3, 4)$
$-V_{\{(1)_2\}\{(1)_2\}}^{(E,E)_2 A_2 A_1 A_1(A_2)}$		$\frac{i}{\sqrt{2}}(a_{2a}^+ a_{2b} - a_{2b}^+ a_{2a})$
$+V_{\{(1)_2\}\{(1)_2\}}^{(E,E)_2 E A_1 A_1(A_1)}$	a	$-\frac{1}{\sqrt{2}}(a_{2a}^+ a_{2a} - a_{2b}^+ a_{2b})$
	b	$\frac{1}{\sqrt{2}}(a_{2a}^+ a_{2b} + a_{2b}^+ a_{2a})$
$+V_{\{(1)_3\}\{(1)_3\}}^{(F_2, F_2)_3 A_1 F_2 A_1 F_2(F_2)}$	x^a	$-\frac{1}{\sqrt{2}}(a_{3y}^+ a_{3z} + a_{3z}^+ a_{3y})$
$+V_{\{(1)_3\}\{(1)_3\}}^{(F_2, F_2)_3 A_1 E A_1 E(E)}$	a	$\frac{1}{\sqrt{6}}(a_{3x}^+ a_{3x} + a_{3y}^+ a_{3y} - 2a_{3z}^+ a_{3z})$
	b	$-\frac{1}{\sqrt{2}}(a_{3x}^+ a_{3x} - a_{3y}^+ a_{3y})$
$-V_{\{(1)_3\}\{(1)_3\}}^{(F_2, F_2)_3 A_1 F_1 A_1 F_1(F_1)}$	x^a	$-\frac{i}{\sqrt{2}}(a_{3y}^+ a_{3z} - a_{3z}^+ a_{3y})$
$+V_{\{(1)_3\}\{(1)_3\}}^{(F_2, F_2)_3 A_1 F_2 A_1 F_2(F_2)}$	x^a	$-\frac{1}{\sqrt{2}}a_{3x}^+ a_{3x} (a_{3y}^+ a_{3z} + a_{3z}^+ a_{3y})$
$+V_{\{(1)_3\}\{(1)_3\}}^{(F_2, F_2)_3 A_1 A_1 A_1(A_1)}$		$\frac{1}{\sqrt{3}}(a_{3x}^+ a_{3x} a_{3y}^+ a_{3y} + a_{3x}^+ a_{3x} a_{3z}^+ a_{3z} + a_{3y}^+ a_{3y} a_{3z}^+ a_{3z})$
$+V_{\{(2)_2\}\{(2)_2\}}^{(E,E)_2 A_1 A_1 A_1(A_1)}$		$\frac{\sqrt{2}}{16} \left((a_{2a}^{+3} a_{2a}^3 + a_{2b}^{+3} a_{2b}^3 + a_{2a}^+ a_{2a} a_{2b}^{+2} a_{2b}^2 + a_{2a}^{+2} a_{2a}^2 a_{2b}^+ a_{2b}) \right.$ $\left. + (a_{2a}^{+3} a_{2a}^+ a_{2b}^2 + a_{2a}^{+2} a_{2b}^+ a_{2b}^3 + h.c.) \right)$
$-V_{\{(1)_3\}\{(1)_3\}}^{(F_2, F_2)_3(A_1, F_2)_4 A_1 F_2 F_2(F_1)}$	x^a	$-\frac{i}{\sqrt{2}}a_{4x}^+ a_{4y} a_{3z}^+ (a_{3x}^+ a_{3z}^+ a_{3y} - a_{3x}^+ a_{3y}^+ a_{3z}) + h.c.$
$-V_{\{(1)_2\}\{(1)_4\}}^{(E, A_1)_2(A_1, F_2)_4 E A_1 F_2 F_2(F_2)}$	x	$-\frac{1}{2}a_{2a}^+ a_{4x} + \frac{\sqrt{3}}{2}a_{2b}^+ a_{4x} + h.c.$
	y	$-\frac{1}{2}a_{2a}^+ a_{4y} - \frac{\sqrt{3}}{2}a_{2b}^+ a_{4y} + h.c.$
	z	$a_{2a}^+ a_{4z} + h.c.$

^ay and z components are deduced from the x component by a circular permutation of x, y, z.

in a symmetrized form adapted to the T_d point group. As explained in Ref. 65 for symmetric tops, the t parameters are related in a systematic way to the h parameters in Eq. (20) using symbolic Maple computer programs through a two-step process. This consists in solving recursively a linear system of equations with t as unknowns. Through this procedure the non-empirical t parameters are numerically determined directly from the geometry of the molecule and from the PES whatever the order the Hamiltonian is. As also pointed out in Ref. 65, these parameters could be determined analytically from the spectroscopic constants ω , $\zeta_{k\sigma, l\sigma'}$, B_e , $B_{k\sigma}^{\alpha\beta}$, $B_{k\sigma l\sigma'}^{\alpha\beta}$, ... with the aid of symbolic calculations. Some low orders in the ITO vibration-rotation Hamiltonian have been considered in Ref. 47. Our techniques allow building the full normal mode ITO model up to any required order. To illustrate this method we give an example of Coriolis and centrifugal distortion terms which contain first and second power of the total angular momentum components. For an illustration we voluntarily limit ourself only to the leading interaction terms to avoid too extensive expressions. So the first Coriolis vibration-rotation interaction terms $H_{\text{Cor}} = -2\sum_{\alpha} B_e \pi_{\alpha} J_{\alpha} + \dots$ can be written as

$$\begin{aligned}
 H_{\text{Cor}} = & \frac{6B_e}{\sqrt{2}} \zeta_{3y, 3z}^x \left(-V_{\{(1)_3\}\{(1)_3\}}^{(F_2, F_2)_3 A_1 F_1 A_1 F_1(F_1)} \otimes \mathbf{R} \right)^{(A_1)} \\
 & + \frac{6B_e}{\sqrt{2}} \zeta_{4y, 4z}^x \left(-V_{\{(1)_4\}\{(1)_4\}}^{(F_2, F_2)_4 A_1 A_1 F_1 F_1(F_1)} \otimes \mathbf{R} \right)^{(A_1)} \\
 & - \sqrt{2} \zeta_{3z, 4y}^x \Delta_{43}^+ \left(-V_{\{(1)_3\}\{(1)_4\}}^{(F_2, A_1)_3(A_1, F_2)_4 A_1 F_2 F_2(F_1)} \otimes \mathbf{R} \right)^{(A_1)} \\
 & + \sqrt{2} \zeta_{3z, 4y}^x \Delta_{43}^- \left(-V_{\{(1)_3\}\{(1)_4\}\{0\}}^{(F_2, A_1)_3(F_2, A_1)_4 A_1 F_2 F_2(F_1)} \otimes \mathbf{R} \right)^{(A_1)}
 \end{aligned}$$

$$\begin{aligned}
 & - \zeta_{2b, 3z}^z \Delta_{32}^+ \left(-V_{\{(1)_2\}\{(1)_3\}}^{(E, A_1)_2(A_1, F_2)_3 E F_2 A_1 F_2(F_1)} \otimes \mathbf{R} \right)^{(A_1)} \\
 & + \zeta_{2b, 3z}^z \Delta_{32}^- \left(-V_{\{(1)_2\}\{(1)_3\}\{0\}}^{(E, A_1)_2(F_2, A_1)_3 E F_2 A_1 F_2(F_1)} \otimes \mathbf{R} \right)^{(A_1)} \\
 & - \zeta_{2b, 4z}^z \Delta_{42}^+ \left(-V_{\{(1)_2\}\{(1)_4\}}^{(E, A_1)_2(A_1, F_2)_4 E A_1 F_2 F_2(F_1)} \otimes \mathbf{R} \right)^{(A_1)} \\
 & + \zeta_{2b, 4z}^z \Delta_{42}^- \left(-V_{\{(1)_2\}\{(1)_4\}\{0\}}^{(E, A_1)_2(F_2, A_1)_4 E A_1 F_2 F_2(F_1)} \otimes \mathbf{R} \right)^{(A_1)} \\
 & + \dots, \tag{28}
 \end{aligned}$$

where $\Delta_{ij}^{\varepsilon'} = \frac{6B_e}{8}(\sqrt{\omega_i/\omega_j} + \varepsilon' \sqrt{\omega_j/\omega_i})$ and $\mathbf{R} \equiv R^{1(1, F_1)}$. In a similar fashion the centrifugal distortion part $H_{\text{Cent}} = \sum_{\alpha} B_{\alpha}^e J_{\alpha}^2 + \sum_{\alpha\beta, k\sigma} B_{k\sigma}^{\alpha\beta} q_{k\sigma}^{(\Gamma)} J_{\alpha} J_{\beta} + \dots$ can be cast into the form

$$\begin{aligned}
 H_{\text{Cent}} = & B_e \left(+V_{\{0\}\{0\}}^{A_1 A_1 A_1 A_1(A_1)} \otimes R^{2(0, A_1)} \right)^{(A_1)} \\
 & - \frac{3B_1^{zz}}{8\sqrt{6}} \left(+V_{\{(1)_1\}\{0\}}^{A_1 A_1 A_1 A_1(A_1)} \otimes R^{2(0, A_1)} \right)^{(A_1)} \\
 & - \frac{3B_{3z}^{xy}}{8} \left(+V_{\{(1)_3\}\{0\}}^{(F_2, A_1)_3 A_1 F_2 A_1 F_2(F_2)} \otimes R^{2(2, F_2)} \right)^{(A_1)} \\
 & - \frac{3B_{4z}^{xy}}{8} \left(+V_{\{(1)_4\}\{0\}}^{(F_2, A_1)_4 A_1 A_1 F_2 F_2(F_2)} \otimes R^{2(2, F_2)} \right)^{(A_1)} \\
 & - \frac{B_{2b}^{yy}}{4} \left(+V_{\{(1)_2\}\{0\}}^{(E, A_1)_2 E A_1 A_1(A_1)} \otimes R^{2(2, E)} \right)^{(A_1)} \\
 & + \dots. \tag{29}
 \end{aligned}$$

The efficiency of the method proposed here lies in the drastic reduction of the number of terms in the Hamiltonian when using the ITO formalism. This is clearly indicated in

TABLE III. Reduction of the number of rovibrational terms corresponding to a usual truncation of the Taylor series Hamiltonian expansion for XY_4 molecules when using the ITO formalism. The number of purely vibrational terms is given in the parenthesis. H_{polyad} corresponds to a tensor Hamiltonian expansion in the polyad approximation corresponding to $\omega_1 : \omega_2 : \omega_3 : \omega_4 \approx 2 : (1 : 1) : (2 : 2 : 2) : (1 : 1 : 1)$.

Order	Number of H_{Watson} terms Eq. (20)		Number of H_{tensor} terms Eq. (27)	Number of H_{polyad} ITO block-diagonal terms
4	1490 (871)	→	328 (223)	61 (39)
5	7799 (3904)	→	1481 (866)	195 (100)
6	35 933 (16 074)	→	6 252 (3242)	768 (347)
7	142 757 (57 434)	→	23 548 (10 954)	2510 (971)
8	515 098 (189 855)	→	81 538 (34 656)	8301 (2859)
9	1 684 813 (572 318)	→	259 593 (101 835)	24 843 (7534)
10	5 118 269 (1 619 267)	→	770 354 (281 837)	71 737 (19 562)

Table III where the number of terms increases very rapidly with the order. The order of the Hamiltonian expansion is defined as $m + n$ where m is the power in the elementary vibrational operators and n is the power of the total angular momentum operators. The number of invariant tensor operators can also be calculated by the generating function approach.⁴⁸ The corresponding Hamiltonian and potential are denoted by $H^{(m+n)}$ and $U^{(m)}$, respectively. For example, at order 6 there is six times more terms in the “usual” Watson Hamiltonian than in the full tensor Hamiltonian. Consequently, the use of ITOs turns out to be really advantageous for studying high-symmetric systems such as spherical top molecules. For a comparison with effective ITO Hamiltonians which are often used for empirical fits of spectroscopic data, we also give the number of terms in frame of the polyad approximation in the last column of Table III. It is clear that the number of vibrational H terms in effective models is much smaller, though additional rotational terms associated with higher J^n powers (with $n > 2$) appear. But this approach, based on the perturbation theory, is beyond the scope of the present paper. Our variational calculations directly account for inter-polyads interactions.

III. ENERGY SPECTRUM CALCULATIONS

As already stated above, all calculations were performed using the recent NRT potential⁴⁵ for three T_d methane species: $^{12}\text{CH}_4$, $^{13}\text{CH}_4$, and $^{12}\text{CD}_4$. The (ro)vibrational energy levels were computed variationally using the parallelized MIRS computer package initially designed to effective Hamiltonian models⁵⁷ but recently extended to *ab initio* Hamiltonians in the normal mode approach.⁵⁸ Due to the lack of detailed experimental spectra of methane for higher polyads, purely empirical models employed during the past decades cannot properly describe resonance parameters associated with unobserved dark states. This is true, for example, for the $P = 2(v_1 + v_3) + v_2 + v_4 = 4$ polyad (called tetradecad) where analyses⁵⁹ are not yet completely finished. A way to get round the problem is the use of PESs with the model (27) where all resonances are inherently accounted for in a systematic way. Technically a sophisticated analytical form of the NRT PES was transformed in rectilinear, normal coordinates, and expanded in 10th order with the atomic masses m_H

$= 1.007825$ u, $m_D = 2.014108$ u and $m_{\text{C13}} = 13.003355$ u. As far as the kinetic energy operator is concerned, a detailed study suggests that for vibrational calculations it is sufficient to expand the reciprocal inertia tensor at order 6. The maximum powers of the vibrational expansion in the term $\pi^\dagger \mu \pi$ are equal to 10. Convergence of the potential $U(q)$ and μ -tensor will be discussed in more details below.

A. Vibrational basis set

The first step of the calculations concerns a computation of the $J = 0$ Hamiltonian eigenvalues. The evaluation of the vibrational energy levels requires a set a primitive wavefunctions which is arranged according to the same coupling scheme as for operators (27). Our initial basis set is built as a tensor product of four harmonic oscillator normal mode functions

$$|((\Psi_{v_1}^{(A_1)} \otimes \Psi_{v_2}^{(C_2)})^{(C_2)} \otimes (\Psi_{v_3}^{(C_3)} \otimes \Psi_{v_4}^{(C_4)})^{(C_{34})})_{\sigma_v}^{(C_v)}\rangle, \quad (30)$$

and the matrix elements (ME) are computed by using the Wigner-Eckart theorem

$$\langle \Psi_{\sigma'}^{(C')} | T_{\sigma_0}^{(C_0)} | \Psi_{\sigma}^{(C)} \rangle = F \begin{pmatrix} C_0 & C & C' \\ \sigma_0 & \sigma & \sigma' \end{pmatrix} \langle C' || T^{(C_0)} || C \rangle, \quad (31)$$

where $\langle \cdot \cdot \cdot || \cdot \cdot \cdot || \cdot \cdot \cdot \rangle$ are reduced matrix elements. Note that all useful expressions concerning tensor and ME calculations can be found in Ref. 50. It is obvious that the account of symmetry makes the calculation less demanding for time and memory: for T_d molecules the Hamiltonian matrix is decomposed into five sub-blocks A_1, A_2, E, F_1 , and F_2 of dimensions $N_{A_1}, N_{A_2}, N_E, N_{F_1}$, and N_{F_2} , respectively.

B. Truncation-reduction scheme

To further reduce the high dimensionality of the 9D vibrational problem, one needs an optimal selection of terms involved in the expansions (27)–(30). In all variational methods for the nuclear motion of polyatomic molecules, some compression-truncation techniques of the primitive basis set are generally applied.^{6,39} Otherwise calculations become unfeasible because of rapidly increasing number of terms.

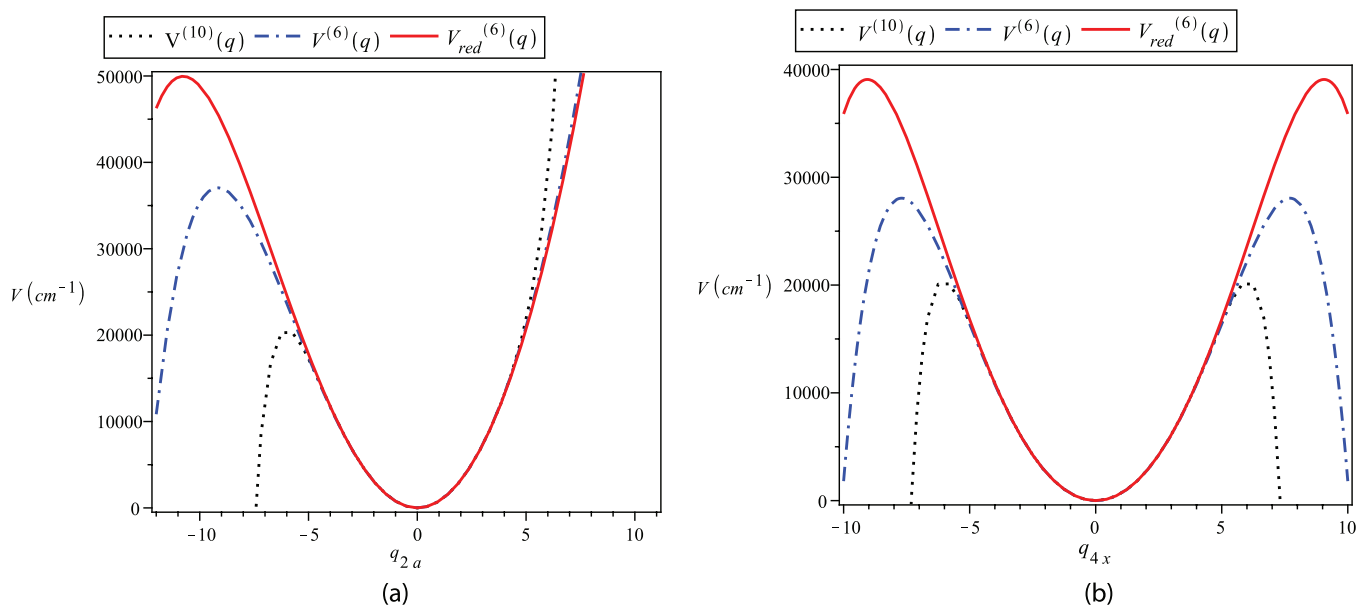


FIG. 1. One dimensional cut of the potential expansions $V_{red}^{(6)}(q)$, $V^{(10)}(q)$, and $V^{(6)}(q)$ (see Eq. (35)) as a function of q_{2a} (top figure) and q_{4x} (bottom figure).

Here we propose a new strategy of truncation-reduction technique adapted to our ITO normal mode representation. This applies simultaneously to the Hamiltonian (27) and to the basis set (30) expansions. The purpose is to select the terms in both expansions in a consistent manner that allows to fully use the advantages of the approach, namely, complete account of symmetry properties and very fast calculations of ME via simple analytical relations using (31) without loss of precision. On the other hand this procedure aims at minimizing the cost of the calculations and reducing the impacts of well-known drawbacks of Taylor series expansions at large distances.

Let us denote \mathcal{F} a finite dimension subspace of the full Hilbert space of vibrational states spanned by a selected set of normal mode basis functions (30). For a given basis function (30), every term in our ITO vibrational Hamiltonian model (21)–(25) generates a limited number of non-vanishing off-diagonal coupling elements, which is directly related to the order of the term. This follows immediately from examples given in Table II and from the well-known relations for the matrix elements of a^+ , a operators. It is thus natural to introduce a first cut-off criterium

$$\sum_i v_i \leq v_{max}, \quad (32)$$

with $v_i = 0, \dots, v_{max}$, defining the subspaces $\mathcal{F}(v_{max})$. The v_{max} values will correlate with the maximum order of the Hamiltonian expansion in Eqs. (21), (25), and (27).

The use of Taylor series normal mode expansion of the Hamiltonian simplifies ME calculations but induces two specific issues. In order to converge calculations, one first needs achieving accurate representation of the kinetic operator and of PES by a truncated expansion in the range of nuclear configurations \mathcal{R} spanned by wavefunctions belonging to \mathcal{F} . Our experience showed that in order to converge calculations of 5 or 6 vibrational quanta to the precision of $\sim 1 \text{ cm}^{-1}$ one would need 8th or 10th order of the Hamiltonian expansion.

First, the number of tensor operators involved in the complete nuclear normal-mode Hamiltonian expansion drastically grows as the order increases (see Table III). This means that the computation of converged energy levels becomes more and more intractable for practical applications. Second, a lack of reliability arises from the incorrect asymptotic behaviour of a polynomial PES representation. It is well-known that a truncated Taylor series expansion can produce spurious minima and artificial barriers and can go down more and more sharply to $(-\infty)$ with the increasing order of the polynomial (Fig. 1). Wavefunctions (30) belonging to \mathcal{F} die out exponentially outside \mathcal{R} range of nuclear configurations. If these artifacts are beyond the \mathcal{R} range, they do not impact the vibration calculations. In order to converge high- v calculations, one needs to increase the order of the Hamiltonian and to enlarge the \mathcal{F} subspace of basis functions (30). Consequently the nuclear configuration subspace \mathcal{R} should also be enlarged and basis functions may probe artifacts of a standard Taylor series truncations. In this case the quality of variational calculations rapidly deteriorates as the size of the basis increases. Some questions are raised in Ref. 77 about the description of bound states when non-physical regions occur in the PES.

To get around these difficulties we have modified the usual procedure of Taylor series truncation resulting in a reduction of poorly behaving terms in the Hamiltonian expansion. This truncation-reduction procedure which has been successfully applied to tetratomic molecules in Ref. 65, is threefold. That allows (i) to deal with lower orders and thus to reduce the number of tensor operators making the Hamiltonian matrix sparse, (ii) to describe accurately low-lying molecular states without almost no loss of precision, and (iii) to better compute converged energy levels using more smoothly behaving potential over a wider range of nuclear configurations.

The key feature of the method is to introduce an additional intermediate cut-off through a m -criterion for a n th

are given by: $\text{rms}(\mu_6 - \mu_0) = 0.8 \text{ cm}^{-1}$, $\text{rms}(\mu_6 - \mu_2) = 1.9 \times 10^{-2} \text{ cm}^{-1}$ and $\text{rms}(\mu_6 - \mu_4) = 4.9 \times 10^{-4} \text{ cm}^{-1}$. Considering the accuracy of *ab initio* PESs, these comparisons prove that a 2nd order μ -tensor expansion would be sufficient for vibrational calculations in the considered energy range. In order to have security margins, we kept the μ_4 -expansion in the kinetic model of our calculations.

The timing and storage requirements for $J = 0$ are as follows: computation of the matrix elements for the five blocks using the $\mathcal{F}(9)$ basis and for the 6252 operators in the Hamiltonian takes few hours on a standard quad core Intel desktop

computer while the diagonalization takes 10 min. The sizes of the corresponding matrix element and eigenvector files are 700 MB and 600 MB and so are relatively small compared to those involved in Lanczos-type procedures, for example.

It is instructive to compare our variational normal mode energy levels to those obtained from the same PES but using curvilinear coordinates and the exact kinetic energy operator—without using Taylor series expansions—as presented in Ref. 45. The convergence of our calculated levels with respect to the variational calculation in curvilinear coordinates are given in Table V according to various

TABLE V. Convergence of the Hamiltonian (27) for selected vibrational energy levels of $^{12}\text{CH}_4$ and rms deviations (cm^{-1}) using normal modes with the $\mathcal{F}(9)$ basis and with various truncation schemes.

Polyad	$v_1 v_2 v_3 v_4$	Sym (Mult)	E (Ref. 45) (cm^{-1}) ^a	$\Delta E = E^a - E(\text{our})^b$ (cm^{-1})			
				Orders n	$n \rightarrow m$	n	$n \rightarrow m$
				6	8 \rightarrow 6 ^c	10	10 \rightarrow 6 ^c
P1	0001	F_2	1310.76	-1.54	0.38	-0.10	-0.10
	0100	E	1533.33	-1.13	0.46	-0.13	-0.14
P2	0002	A_1	2587.12	-7.00	2.36	-1.17	-0.45
	0002	F_2	2614.24	-4.86	0.95	-0.59	-0.18
	0002	E	2624.72	-3.39	1.20	-0.37	-0.29
	0101	F_2	2830.48	-4.48	2.22	-0.81	-0.49
	0101	F_1	2846.04	-3.21	1.22	-0.37	-0.27
	1000	A_1	2916.48	-1.05	-0.05	0.08	0.12
	0010	F_2	3019.50	-0.77	0.02	0.00	-0.02
	0200	A_1	3063.79	-3.40	1.78	-0.61	-0.51
	0200	E	3065.17	-2.70	1.29	-0.41	-0.37
P3	0003	$F_2(1)$	3870.76	-15.88	3.97	-4.10	-0.78
	0003	A_1	3909.18	-11.66	0.36	-2.41	0.21
	0003	F_1	3920.53	-8.10	1.94	-0.99	-0.03
	0003	$F_2(2)$	3931.22	-7.38	2.12	-1.27	-0.43
	0102	$E(1)$	4101.78	-12.85	5.95	-3.51	-1.60
	0102	F_1	4129.00	-9.88	3.92	-2.15	-0.83
	0102	A_1	4133.38	-8.92	4.87	-2.14	-1.12
	0102	F_2	4142.93	-8.30	2.78	-1.57	-0.44
	0102	$E(2)$	4151.38	-6.50	2.83	-1.07	-0.52
	0102	A_2	4161.95	-5.46	2.33	-0.72	-0.38
	1001	F_2	4223.63	-4.00	-0.01	0.16	-0.05
	0011	F_2	4319.37	-3.14	0.14	0.03	-0.15
	0011	F_1	4322.66	-3.43	-0.33	-0.57	-0.94
	0011	E	4322.67	-3.30	-0.08	-0.05	-0.49
	0011	A_1	4323.03	-3.08	0.94	-0.24	-0.13
	0201	$F_2(1)$	4349.13	-9.28	5.48	-2.60	-1.37
	0201	F_1	4363.83	-6.74	3.45	-1.32	-0.72
	0201	$F_2(2)$	4379.08	-5.87	2.74	-1.03	-0.57
	1100	E	4435.22	-2.67	0.39	-0.07	-0.20
	0110	F_1	4537.62	-2.39	0.39	-0.15	-0.36
	0110	F_2	4543.94	-2.68	0.65	-0.28	-0.44
	0300	E	4592.43	-6.42	3.72	-1.50	-0.98
	0300	A_2	4595.38	-4.66	2.52	-0.81	-0.60
	0300	A_1	4595.66	-4.85	2.45	-0.96	-0.60
rms (up to P3)^d				6.50	2.49	1.40	0.61
rms (up to P4)^d				10.90	3.85	3.31	0.84

^aVariational calculations with internal non-linear coordinate by Nikitin *et al.*⁴⁵ obtained from the same PES without power series expansion and using the exact kinetic operator.

^b $E(\text{our})$ are the eigenvalues of the ITO normal-mode Hamiltonian (27) using our variational calculations.

^cNotation 8 \rightarrow 6 (respectively, 10 \rightarrow 6) corresponds to the truncation-reduction scheme of Sec. III B; this means that the Hamiltonian is expanded up to 8th (respectively, 10) power in q and converted to 6th power in a^\pm , a .

^dRoot-mean-squares for $E^a - E^b(\text{our})$ for energy levels up to the third (P3: octad) and fourth (P4: tetradecad) polyads. The total number of vibrational sublevels is 35 up to P3 and 95 up to P4.

TABLE VI. Vibrational energy levels up to the tetradecad of $^{12}\text{CH}_4$, $^{13}\text{CH}_4$, and $^{12}\text{CD}_4$ computed variationally with the $\mathcal{F}(9)$ basis and using $H_{\text{red}}^{(6)}$ ITO normal mode model. $E(\text{O-C}) = (\text{observed-calculated})$ and rms deviations are given in cm^{-1} .

$^{12}\text{CH}_4$					$^{13}\text{CH}_4$			$^{12}\text{CD}_4$				
$v_1 v_2 v_3 v_4$	Sym	E	O-C	(%)	E	O-C	(%)	$v_1 v_2 v_3 v_4$	Sym	E	O-C	(%)
0001	F_2	1310.66	0.10	96	1302.69	0.09	96	0001	F_2	997.68	0.19	98
0100	E	1533.19	0.14	96	1533.36	0.14	96	0100	E	1091.61	0.04	98
0002	A_1	2586.67	0.37	90	2571.77	0.33	90	0002	A_1	1965.09	0.10	79
0002	F_2	2614.06	0.20	94	2598.46	0.18	94	0002	F_2	1990.07	0.40	96
0002	E	2624.43	0.19	98	2608.58	0.16	98	0002	E	1996.49	0.34	98
0101	F_2	2829.99	0.33	90	2822.14	0.30	90	0101	F_2	2083.23	0.16	94
0101	F_1	2845.77	0.30	96	2837.92	0.29	96	0101	F_1	2090.61	0.27	98
1000	A_1	2916.60	-0.12	79	2915.55	-0.11	79	1000	A_1	2101.35	0.03	71
0010	F_2	3019.52	-0.03	83	3009.57	0.02	83	0200	A_1	2182.11	0.05	96
0200	A_1	3063.29	0.36	96	3063.62	0.34	96	0200	E	2182.48	0.10	98
0200	E	3064.80	0.34	96	3065.13	0.33	96	0010	F_2	2260.11	-0.03	88
0003	$F_2(1)$	3869.98	0.51	48	3847.94		48	0003	$F_2(1)$	2942.46		38
0003	A_1	3909.40	-0.20	88	3886.58		88	0003	A_1	2976.28		90
0003	F_1	3920.50	0.01	92	3897.38		94	0003	F_1	2983.40		94
0003	$F_2(2)$	3930.79	0.13	53	3907.41		53	0003	$F_2(2)$	2989.50		48
0102	$E(1)$	4100.18	1.21	74	4085.38		74	0102	$E(1)$	3048.81		72
0102	F_1	4128.17	0.59	86	4112.61		86	0102	F_1	3073.71		90
0102	A_1	4132.26	0.60	86	4116.41		86	0102	A_1	3077.22		92
0102	F_2	4142.49	0.37	90	4127.03		92	0102	F_2	3079.90		92
0102	$E(2)$	4150.86	0.35	83	4135.24		83	0102	$E(2)$	3084.42		92
0102	A_2	4161.58	0.26	98	4145.79		98	0102	A_2	3090.74		98
1001	F_2	4223.58	-0.12	77	4213.92		77	1001	F_2	3103.56		66
0011	F_2	4319.23	-0.02	83	4301.32		83	0201	$F_2(1)$	3168.06		46
0011	F_1	4321.72	0.87	81	4304.17		81	0201	F_1	3175.33		94
0011	E	4322.18	0.00	81	4304.33		81	0201	$F_2(2)$	3182.58		49
0011	A_1	4322.90	-0.20	76	4305.04		76	1100	E	3186.02		71
0201	$F_2(1)$	4347.76	0.96	44	4339.98		44	0011	E	3250.83		88
0201	F_1	4363.11	0.50	90	4355.39		90	0011	F_2	3252.69		88
0201	$F_2(2)$	4378.51	0.44	49	4370.77		49	0011	F_1	3253.11		86
1100	E	4435.02	0.10	77	4434.06		79	0011	A_1	3254.13		83
0110	F_1	4537.26	0.29	83	4527.61		83	0300	E	3271.76		96
0110	F_2	4543.50	0.26	77	4533.79		77	0300	A_2	3272.59		98
0300	E	4591.45	0.58	94	4591.95		94	0300	A_1	3272.72		98
0300	A_2	4594.78	0.49	96	4595.27		96	0110	F_1	3343.15		88
0300	A_1	4595.06	0.45	96	4595.55		96	0110	F_2	3346.16		85
0004	$A_1(1)$	5122.20	-0.86	40	5093.73		41	1002	A_1	3895.31		31
0004	$F_2(1)$	5144.11	-0.87	59	5115.22		61	0004	$F_2(1)$	3914.10		53
0004	$E(1)$	5167.49	-0.33	56	5138.15		56	0004	$E(1)$	3928.01		49
0004	$F_2(2)$	5212.46	-1.17	66	5182.43		66	0004	$F_2(2)$	3966.01		69
0004	$E(2)$	5229.72	-0.81	61	5199.21		61	0004	$E(2)$	3976.60		67
0004	F_1	5231.61	-0.83	90	5200.99		90	0004	F_1	3978.63		92
0004	$A_1(2)$	5241.18	-1.20	52	5210.35		52	0004	A_1	3983.71		49
0103	$F_2(1)$	5370.03	0.49	45	5348.13		45	0103	$F_2(1)$	4019.23		40
0103	$F_1(1)$	5389.23	0.44	55	5367.24		55	0103	$F_1(1)$	4029.11		45
0103	E	5425.05	-0.39	79	5402.31		79	0103	E	4060.63		83
0103	$F_2(2)$	5429.84	-0.26	40	5406.47		38	0103	$F_2(2)$	4065.73		58
0103	$F_1(2)$	5437.65	-0.86	74	5414.62		74	1002	A_1	4066.51		29
0103	$F_2(3)$	5444.91	0.21	42	5421.93		44	0103	$F_1(2)$	4067.76		79
0103	$F_1(3)$	5463.18	-0.26	59	5439.92		59	0103	$F_2(3)$	4071.94		38
1002	A_1	5494.09		61	5477.30		62	0103	$F_1(3)$	4080.94		48
1002	F_2	5522.63		74	5504.81		74	1002	F_2	4097.94		62
1002	E	5533.83		74	5515.69		76	1002	E	4106.34		62
0012	$F_2(1)$	5588.91	-0.88	72	5564.34		74	0202	$A_1(1)$	4130.00		62
0012	A_1	5604.80		40	5583.77		64	0202	$E(1)$	4132.37		66
0202	$A_1(1)$	5612.58		56	5590.70		74	0202	$F_2(1)$	4156.93		44
0202	$E(1)$	5613.02		52	5590.88		71	0202	$E(2)$	4162.59		46
0012	$F_1(1)$	5615.95		76	5591.98		69	0202	F_1	4162.98		86

TABLE VI. (Continued.)

$^{12}\text{CH}_4$					$^{13}\text{CH}_4$			$^{12}\text{CD}_4$				
$v_1 v_2 v_3 v_4$	Sym	E	O–C	(%)	E	O–C	(%)	$v_1 v_2 v_3 v_4$	Sym	E	O–C	(%)
0012	$F_2(2)$	5616.09		71	5593.94		50	0202	$F_2(2)$	4168.12		41
0012	E	5619.12		64	5599.41		55	0202	A_2	4168.72		92
0012	$F_1(2)$	5626.17		74	5600.47		72	0202	$A_1(2)$	4173.48		81
0012	$F_2(3)$	5627.34		74	5601.94		76	0202	$E(3)$	4180.76		49
0202	$F_2(1)$	5641.81	1.64	38	5626.15		40	1101	F_2	4182.50		58
0202	$E(2)$	5653.48	0.65	46	5637.88		46	2000	A_1	4190.62		42
0202	F_1	5655.39	–0.51	83	5639.90		83	1101	F_1	4190.73		64
0202	A_2	5663.59	0.29	85	5647.96		85	0012	$F_2(1)$	4212.82		66
0202	$F_2(2)$	5668.55	0.05	44	5653.28		44	0012	$F_1(1)$	4238.68		88
0202	$A_1(2)$	5681.65	2.76	69	5666.27		69	0012	A_1	4239.47		77
0202	$E(3)$	5691.20	0.28	50	5675.57		50	0012	$F_2(2)$	4239.82		72
1101	F_2	5727.41		69	5717.72		71	0012	E	4241.61		81
1101	F_1	5745.21		76	5735.52		77	0012	$F_2(3)$	4246.05		77
2000	A_1	5791.62	–1.37	44	5785.83		40	0012	$F_1(2)$	4246.99		85
0111	$F_2(1)$	5824.14	–1.04	30	5806.70		31	0301	$F_2(1)$	4252.25		64
0111	$F_1(1)$	5825.50		56	5807.82		58	0301	$F_1(1)$	4259.43		67
0111	$E(1)$	5832.01		40	5814.59		38	0301	$F_2(2)$	4266.66		72
0111	A_1	5834.92		59	5819.29		58	1200	A_1	4269.92		66
0111	$E(2)$	5842.58		79	5825.30		79	1200	E	4270.25		69
0111	A_2	5842.75		45	5825.24		45	0301	$F_1(2)$	4273.66		71
0111	$F_2(2)$	5844.21	–0.21	49	5826.76		50	1010	F_2	4329.69		22
0111	$F_1(2)$	5847.30		52	5829.59		52	0111	$F_1(1)$	4330.34		53
1010	F_2	5860.85		32	5849.83		32	0111	$E(1)$	4331.34		62
0301	$F_2(1)$	5867.01	0.65	27	5857.51		48	0111	A_1	4332.30		76
0301	$F_1(1)$	5879.03	–0.01	61	5871.41		61	0111	$F_2(1)$	4333.25		32
0301	$F_2(2)$	5894.19	–0.07	69	5886.57		69	0111	A_2	4335.29		88
0301	$F_1(2)$	5909.01	0.70	69	5901.38		69	0111	$E(2)$	4337.64		62
0020	A_1	5939.74		48	5930.38		36	0111	$F_2(2)$	4339.54		55
1200	E	5952.53	–0.09	77	5951.66		79	0111	$F_1(2)$	4340.47		50
1200	A_1	5968.64		36	5960.31		49	0400	A_1	4360.13		94
0020	F_2	6004.92	–0.23	55	5987.34		55	0400	$E(1)$	4360.73		94
0020	E	6044.14	–0.27	72	6024.07		72	0400	$E(2)$	4362.32		96
0210	$F_2(1)$	6054.59	0.05	40	6044.90		42	0210	$F_2(1)$	4424.70		55
0210	F_1	6060.50	0.15	77	6051.08		77	0210	F_1	4428.68		85
0210	$F_2(2)$	6065.56	–0.24	40	6055.96		41	0210	$F_2(2)$	4430.92		53
0400	A_1	6116.29	0.46	92	6116.96		92	0020	A_1	4461.26		72
0400	$E(1)$	6118.14	0.48	94	6118.81		94	0020	F_2	4493.88		72
0400	$E(2)$	6123.95	0.22	96	6124.61		96	0020	E	4523.90		79
rms (up to P2)			0.25				0.23					0.20
rms (up to P3)			0.43									
rms (up to P4)			0.64									

truncation schemes for the Hamiltonian. Despite well-known difficulties related to asymptotic behaviour of the polynomial PES approximation, the normal mode variational calculations using our truncation-reduction technique show quite good agreement with the final errors corresponding to the precision of the potential function.⁴⁵ In Table VI the vibrational levels are given up to the fourth polyad and are compared with experimental data when these latter ones are available. These final calculations were done by using the $H(10 \rightarrow 6)$ reduction technique which allows improving substantially the behaviour of the expansions far from equilibrium and reducing drastically the number of operators, without degrading the quality of the model near the reference geometry. At the same time, this made possible to keep advantage of the simple Heisenberg-Weyl (a^+ , a) algebra.

These rms deviations between calculated and observed levels for $^{12}\text{CH}_4$ are very similar to those obtained with the original NRT calculations.⁴⁵ Also we have obtained for the first time an excellent agreement for available levels of $^{13}\text{CH}_4$ and $^{12}\text{CD}_4$ isotopologues. This confirms the accuracy of the NRT PES (Ref. 45) via an absolutely independent method of calculation.

For $J > 0$, the basis set is written as a tensor product between the vibrational functions defined in (30) and rotational functions as

$$|(\Psi^{(C_v)} \otimes \Psi^{(J,nC_r)})_{\sigma}^{(C)}\rangle, \quad (36)$$

where the rotational part is conveniently symmetrized using Ref. 78. To test the validity of our method for rovibrational states, we have variationally computed the energy levels

for $J = 1$ only. This corresponds to matrices of sizes $N_{A_1}^{J=1} = 5752$, $N_{A_2}^{J=1} = 6340$, $N_E^{J=1} = 12\,092$, $N_{F_1}^{J=1} = 18\,558$, and $N_{F_2}^{J=1} = 17\,970$. The predicted levels for $J = 0$ and 1 up to the tetradecad are available in the supplementary material⁷⁹ where we give three leading terms of normal mode contributions in wave functions. This could provide useful information on possible resonance couplings which have to be included in effective spectroscopic model for high-resolution spectra analyses. Convergence for higher J states requires much more demanding computational efforts and will be the subject of a forthcoming publication.

IV. CONCLUSION

The ITO normal mode formulation of the full rovibrational Hamiltonian was successfully applied for variational calculations of energy levels of methane and its isotopologues for the very first time. Using this formulation as well as the procedure of term reduction, we were able to converge variational calculations of ro-vibrational energy levels for $J = 1$ at least up to the tetradecad ($<6000\text{ cm}^{-1}$). For this, we transformed our recent PES to rectilinear, normal coordinates symmetrized in T_d point group. Then we have transformed in a systematic way each term of the Hamiltonian within the tensorial algebra formalism taking full advantage of the high symmetry of CH_4 . A good agreement with the results of the previous work⁴⁵ for $^{12}\text{CH}_4$ using absolutely independent computational approach based on the exact kinetic energy operator and internal curvilinear coordinates as well as supplementary validation for tetrahedral isotopologues (see Table VI) suggest that the NRT PES represents the most accurate presently available potential function for methane in the considered energy range. In Table VI, the (%) column represents the square of the major normal mode basis component ($\times 100$) in the corresponding eigenfunction. Note that due to a full account of the symmetry using the ITO formalism and due to a new truncation-reduction scheme, we were able to converge variational calculations to the same results but with much less basis functions than in the previous study:⁴⁵ the size of our maximum $J = 0$ block was 6340 compared to 43 837 in Ref. 45. New prediction for $^{13}\text{CH}_4$ and $^{12}\text{CD}_4$ can be useful as initial approximation for band centers in spectra analyses: many assignments as well as accurate modellings of high-resolution bands in this range are still missing. Note that though the calculated levels and rms deviations in Tables V and VI, and in supplementary material are ranged for convenience according to the polyad numbers, we did not use the polyad approximation in the Hamiltonian model.

Comparisons given in Tables V and VI and in the supplementary material confirm the validity of the various sequences of transformations in Sec. II and of corresponding computational algorithms that allow systematically building symmetry adapted full normal-mode Hamiltonians to any desired order. Reliable numerical solutions for eigenvalues and eigenfunctions obtained without introducing additional physical assumptions should be useful for further studies. The results of the present work could serve for the validation of new physical and mathematical approaches and simplified mod-

els. In particular, a study of a qualitatively new organization of rovibrational states for much higher polyads of methane is a big challenge (see, for example, Ref. 80 and references therein).

The Hamiltonians (20) and (27) will be used as starting points for the derivation of spectroscopic effective Hamiltonians from the molecular PES using an appropriate formulation of contact transformations (CTs).^{27,47,81} This would result in a re-formulation and simplification of the resonance coupling scheme by introducing the polyad approximation. Good agreement with observations for high J in the ground vibrational state using effective pure rotational Hamiltonian derived from NRT PES was reported in Ref. 82. General CT results for polyad Hamiltonians of methane will be reported in a forthcoming paper.⁸³

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