

# Vibrational Energy Levels via Finite-Basis Calculations Using a Quasi-Analytic Form of the Kinetic Energy

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 Supporting Information

**ABSTRACT:** A variational method for the calculation of low-lying vibrational energy levels of molecules with small amplitude vibrations is presented. The approach is based on the Watson Hamiltonian in rectilinear normal coordinates and characterized by a quasi-analytic integration over the kinetic energy operator (KEO). The KEO beyond the harmonic approximation is represented by a Taylor series in terms of the rectilinear normal coordinates around the equilibrium configuration. This formulation of the KEO enables its extension to arbitrary order until numerical convergence is reached for those states describing small amplitude motions and suitably represented with a rectilinear system of coordinates. A Gauss–Hermite quadrature grid representation of the anharmonic potential is used for all the benchmark examples presented. Results for a set of molecules with linear and nonlinear configurations, i.e., CO<sub>2</sub>, H<sub>2</sub>O, and formyl fluoride (HFCO), illustrate the performance of the method and the versatility of our implementation.

## INTRODUCTION

The use of perturbation theory in second and higher orders has a long tradition in the theoretical prediction and interpretation of vibrational spectra<sup>1,2</sup> and is still extensively applied with new variations and extensions.<sup>3–8</sup> Nevertheless, variational methods constitute a more robust approach for solving the vibrational Schrödinger equation; they overcome the multiple degeneracy or resonance problems associated with the perturbational approach and provide an exact solution to the problem within the constraints imposed by the basis and the potential energy surface (PES) used. The earliest variational developments used a direct-product representation of the wave function in terms of an orthonormal set of basis functions (e.g., harmonic, Morse oscillators, etc.), which has been referred to as finite basis representation (FBR). Pioneer studies in this direction were carried out by Whitehead and Handy,<sup>9,10</sup> Carney et al.,<sup>11–13</sup> and others.<sup>14–15</sup> Other methods applying the FBR approach appeared later, for example, the vibrational self-consistent field (VSCF) method and different ‘CI’ schemes<sup>16–21</sup> as well as some modifications such as parallel vibrational multiple window configuration interaction (P-VMWCI) and the vibrational mean field configuration interaction (VMFCI) approaches.<sup>23</sup> In variational or pseudovariational methods it is also possible to construct a grid-based representation of the wave function, the so-called discrete variable representation (DVR).<sup>23–28</sup> After Light et al.<sup>26–28</sup> had shown the equivalence between FBR and DVR approaches, the latter soon started to be used extensively in almost all fields of nuclear motion theory.<sup>28,29</sup>

The definition and computation of the two components of the nuclear motion Hamiltonian, the kinetic energy and the potential energy operators, are aspects to consider in the theoretical prediction and analysis of vibrational spectra. A choice for

representing the potential energy is a Taylor expansion around a reference configuration (usually the equilibrium structure). This has proven especially suitable for describing regions of the PES near minima, and it is well-suited to the framework of perturbational approaches.<sup>1–5</sup> This representation of the potential can be computed by fitting energy points to an analytic function or alternatively by numerical or analytical calculation of derivatives of the electronic energy.<sup>30,31</sup> Another possibility is to define the potential by a (semi)global PES; this idea provides a better description of areas of the PES other than those close to stationary points. Examples are the work of Braams and co-workers<sup>32–35</sup> as well as the so-called *n*-mode<sup>36–38</sup> and product<sup>39</sup> representations as well as a direct quadrature. The latter has the advantage of providing a diagonal form of the potential energy reducing significantly the computational demand. The choice of coordinates determines the form of the kinetic-energy operator (KEO) and consequently the total Hamiltonian, (assuming that if the coordinate system of the KEO and the potential are different, the transformation between them is known<sup>40</sup>). One option is to express the KEO in curvilinear internal coordinates, (e.g., valence, Jacobi, Radau, or polyspherical coordinates). Some of these coordinates can describe the complete range of eigenstates of a molecule and are suitable for ‘floppy’ molecules and in general for large amplitude vibrational motions. General formulations of the KEO in curvilinear coordinates leading to particularly simple structures have existed for a long time,<sup>41,42</sup> and research in this direction continues.<sup>43–53</sup> However, explicit algebraic expressions of KEOs for some choices of curvilinear coordinates may involve some complexity, especially when

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increasing the molecular size. In these cases, it has been more common to build specific KEOs for molecules with a particular number of atoms (from three to five) and/or atomic arrangements.<sup>54–69</sup> A further possibility is to use rectilinear coordinates, in particular, normal coordinates. Even though they provide a poor description of large amplitude motion, the resulting KEO is unique and can be represented by a compact form.<sup>70,71</sup> These two features make the rectilinear representation attractive when dealing with (semirigid) medium- and large-size molecules and, in general, when attention is placed on low-lying vibrational energy levels and zero-point energy (ZPE), as is the usual case in thermochemical studies as well as the analysis of most infrared spectra. Because of these advantages several investigations have been devoted to Watson's simplified form of the nuclear Hamiltonian in rectilinear normal coordinates, for carrying out either a perturbative treatment<sup>2–5,8</sup> or a variational approach with finite basis<sup>72–83</sup> or discrete variable<sup>40,84–88</sup> representations. Nevertheless, because of complications in factorizing the KEO, the complete Watson Hamiltonian has not always been considered. In the past, this problem has been circumvented by including only the harmonic contribution of the kinetic energy<sup>8,85,86,89–91</sup> or by incorporating only some terms of the KEO beyond the harmonic approximation.<sup>72–75,80–82</sup> So far, the exact KEO has only been considered with numerical integration in the FBR or in the DVR, some examples of the use of these two representations can be found in refs 9–13 and 16–21 (FBR) as well as in refs 40, 84, and 88 (DVR).

In this work, we return to the original work of Whitehead and Handy<sup>10</sup> and describe a vibrational full configuration interaction (VFCI) method in a FBR to calculate energy levels using the complete vibrational Hamiltonian as given by Watson.<sup>70,71</sup> A quadrature grid representation of the anharmonic potential is combined with a quasi-analytic integration of the kinetic energy. The KEO beyond the harmonic oscillator treatment is represented by a Taylor series in rectilinear normal coordinates. We present a formulation of the KEO that allows the expansion to be extended to arbitrary order. Given a highly accurate PES, the applicability of our approach extends to the determination of accurate zero-point energies (ZPE) and low-lying vibrational energy levels. Results for a set of molecules with linear and nonlinear configuration, i.e., CO<sub>2</sub>, H<sub>2</sub>O, and HFCO are presented to illustrate the accuracy of the approach and the applicability of our implementation.

## THEORY

**Vibrational Hamiltonian for Nonlinear and Linear Configurations.** The pure vibrational Hamiltonian (rotational angular momentum equal to zero,  $J = 0$ ) in rectilinear dimensionless normal coordinates ( $q$ ) for a nonlinear molecular system with  $N$  nuclei can be expressed in the following compact form and in units of cm<sup>-1</sup>:<sup>70,92,93</sup>

$$\hat{\mathcal{H}} = \frac{\hbar^2}{2} \sum_{\alpha\beta}^{x,y,z} \hat{\pi}_\alpha \mu_{\alpha\beta} \hat{\pi}_\beta - \frac{\hbar^2}{8} \sum_{\alpha}^{x,y,z} \mu_{\alpha\alpha} + \frac{1}{2} \sum_{k=1}^{3N-6} \omega_k \hat{p}_k^2 + \hat{V}(q) \quad (1)$$

The three first terms of the Hamiltonian define the nuclear kinetic energy,  $\hat{T}(q, \hat{p})$ . The first represents the vibrational Coriolis term, and the second is the kinetic pseudopotential term (traditionally called Watson or  $\hat{U}$  term). The latter has a quantum-mechanical origin and is a small mass-dependent

correction to the vibrational energy that is essentially constant and therefore of little spectroscopic relevance. It can be, however, essential for predicting accurate ZPE necessary, for example, in thermochemical studies.<sup>94</sup>  $\hat{V}(q)$  represents the potential energy surface as a function of the rectilinear dimensionless normal coordinates,  $\omega_k$  is the harmonic frequency for the normal mode  $k$ ,  $\alpha$  and  $\beta$  denote the principal rotational axes ( $A$ ,  $B$ , and  $C$ ). The  $\alpha$ -th component of the effective vibrational angular momentum operator,  $\hat{\pi}_\alpha$  is defined by

$$\hat{\pi}_\alpha = \sum_{kl}^{3N-6} \zeta_{kl}^\alpha \left( \frac{\omega_l}{\omega_k} \right)^{1/2} q_k \hat{p}_l \quad (2)$$

The Coriolis constant,  $\zeta_{kl}^\alpha$ , describes the coupling between the rectilinear normal coordinates  $k$  and  $l$  along the  $\alpha$  axis, and  $\hat{p}_k$  is the linear vibrational momentum conjugate to the reduced dimensionless normal coordinate  $q_k$  and given by  $\hat{p}_k = -i(\partial/\partial q_k)$ . The  $\alpha\beta$ -component of the modified reciprocal inertia tensor  $\mu$  is defined by  $\mu_{\alpha\beta} \equiv (I'^{-1})_{\alpha\beta}$ . Amat and Henry<sup>95,96</sup> derived an expression for  $I'$  which takes the following form for the  $\alpha\beta$ -component:

$$I'_{\alpha\beta} = I_{\alpha\beta}^e + \sum_k^{3N-6} a_k^{\alpha\beta} \gamma_k^{-1/2} q_k + \frac{1}{4} \sum_{kl}^{3N-6} \sum_{\gamma\delta}^{x,y,z} a_k^{\alpha\gamma} I_{\gamma\delta}^{e-1} a_l^{\delta\beta} \gamma_k^{-1/2} \gamma_l^{-1/2} q_k q_l \quad (3)$$

where

$$a_k^{\alpha\beta} = \left( \frac{\partial I_{\alpha\beta}}{\partial Q_k} \right)_e \quad (4)$$

$Q_k$  denotes the mass-weighted rectilinear normal coordinate associated with the normal mode  $k$  and is related to  $q_k$  by  $Q_k = (2\pi c \omega_k / \hbar)^{-1/2} q_k$  ( $\gamma_k = 2\pi c \omega_k / \hbar$ ). Here,  $I^e$  is the moment of inertia at the reference configuration (equilibrium geometry in the present case).

Watson also derived a similar quantum-mechanical expression for linear molecules<sup>71</sup> and avoided the difficulties with the relations between the angular momentum components by transforming the Hamiltonian to the isomorphic form introduced earlier by Hougen.<sup>97</sup> Assuming that the molecular reference configuration lies along the  $z$  axis, the resulting pure vibrational Hamiltonian for linear systems can be written as

$$\hat{\mathcal{H}} = \frac{\hbar^2}{2} \mu (\hat{\pi}_x^2 + \hat{\pi}_y^2) + \frac{1}{2} \sum_{k=1}^{3N-5} \omega_k \hat{p}_k^2 + \hat{V}(q) \quad (5)$$

where,  $\mu = (I')^{-1}$ . For simplicity, the notation is based on:  $\mu = \mu_{xx} = \mu_{yy}$  and  $I' = I'_{xx} = I'_{yy}$ . The components of  $I'$  are defined by

$$I' = I^e{}^{-1} \left( I^e + \frac{1}{2} \sum_k^{3N-5} a_k \gamma_k^{1/2} q_k \right)^2 \quad (6)$$

where the relations  $a_k = a_k^{xx} = a_k^{yy}$  have been exploited. The vibrational Hamiltonian of eqs 1 and 5 can be regrouped in

two parts: the harmonic-oscillator Hamiltonian and the remaining terms. For nonlinear molecules this is

$$\begin{aligned}\hat{\mathcal{H}} &= \hat{\mathcal{H}}_{\text{harm}} + \frac{\hbar^2}{2} \sum_{\alpha\beta} \hat{\pi}_{\alpha} \mu_{\alpha\beta} \hat{\pi}_{\beta} - \frac{\hbar^2}{8} \sum_{\alpha} \mu_{\alpha\alpha} + \hat{V}_{\text{anh}}(q) \\ &= \hat{\mathcal{H}}_{\text{harm}} + \hat{C}_{\text{nonlinear}}(q, \hat{p}) + \hat{U}(q) + \hat{V}_{\text{anh}}(q) \\ &= \hat{\mathcal{H}}_{\text{harm}} + \hat{K}_{\text{nonlinear}}(q, \hat{p}) + \hat{V}_{\text{anh}}(q)\end{aligned}\quad (7)$$

where  $\hat{K}_{\text{nonlinear}}$  contains the vibrational Coriolis and the Watson terms. Similarly, for linear configurations:

$$\begin{aligned}\hat{\mathcal{H}} &= \hat{\mathcal{H}}_{\text{harm}} + \frac{\hbar^2}{2} \mu(\hat{\pi}_x^2 + \hat{\pi}_y^2) + \hat{V}_{\text{anh}}(q) \\ &= \hat{\mathcal{H}}_{\text{harm}} + \hat{C}_{\text{linear}}(q, \hat{p}) + \hat{V}_{\text{anh}}(q) \\ &= \hat{\mathcal{H}}_{\text{harm}} + \hat{K}_{\text{linear}}(q, \hat{p}) + \hat{V}_{\text{anh}}(q)\end{aligned}\quad (8)$$

In both cases, linear and nonlinear configurations,  $\hat{\mathcal{H}}_{\text{harm}}$  is defined by

$$\hat{\mathcal{H}}_{\text{harm}} = \hat{\mathcal{H}}_0 = \frac{1}{2} \sum_{k=1}^{3N-6(5)} \omega_k(q_k^2 + \hat{p}_k^2) \quad (9)$$

The eigenfunctions of  $\hat{\mathcal{H}}_{\text{harm}}$  are one-dimensional harmonic oscillator wave functions,<sup>98</sup>  $\phi_{n_i}[\phi_{n_i} = N_i e^{-q_i^2/2} H_{n_i}(q_i)]$ , where  $H_{n_i}$  is the Hermite polynomial associated to the  $i$ -th normal mode, and the total vibrational molecular wave function,  $\Psi$ , is given by a multidimensional product of harmonic oscillators basis functions (FBR). Use of this ansatz leads to an eigenvalue equation; elements of the corresponding Hamiltonian matrix  $\mathbf{H}$  are given by:

$$H_{KL} = \underbrace{\langle \Psi_K | \hat{\mathcal{H}}_{\text{harm}} | \Psi_L \rangle}_{\delta_{KL} \varepsilon_K} + \underbrace{\langle \Psi_K | \hat{V}_{\text{anh}} | \Psi_L \rangle}_{\text{anharmonic}} + \underbrace{\langle \Psi_K | \hat{K} | \Psi_L \rangle}_{\text{kinetic}} \quad (10)$$

where  $\varepsilon_K$  represents the harmonic energy of the vibrational state  $K$ , and the second and third terms account for the anharmonic contribution and the remaining part of the kinetic energy, respectively. The anharmonic contribution is calculated by multidimensional numerical integration employing Gauss–Hermite quadratures in the FBR,<sup>9–14</sup> and the evaluation of the integrals associated with the kinetic energy operator is discussed in the next section.

$$\begin{aligned}\mu_{(k)}^{(1)} &= \left( \frac{\partial \mu}{\partial Q_k} \right)_e = \mathbf{I}_e^{-1} \mathbf{a} \mathbf{I}_e^{-1} \Rightarrow \mu_{(k)}^{(1)\alpha\beta} \left( \frac{\partial \mu_{\alpha\beta}}{\partial Q_k} \right)_e = - \frac{a_k^{\alpha\beta}}{\mathbf{I}_e^{\alpha\beta} \gamma_k^{1/2}} \\ \mu_{(k,l)}^{(2)} &= \left( \frac{\partial^2 \mu}{\partial Q_k \partial Q_l} \right)_e = \frac{3}{4} \mathbf{I}_e^{-1} \mathbf{a} \mathbf{I}_e^{-1} \mathbf{a} \mathbf{I}_e^{-1} \Rightarrow \mu_{(k,l)}^{(2)\alpha\beta} = \left( \frac{\partial^2 \mu_{\alpha\beta}}{\partial Q_k \partial Q_l} \right)_e = \frac{3}{4} \sum_{\gamma} \frac{a_k^{\alpha\gamma} a_l^{\gamma\beta} + a_l^{\alpha\gamma} a_k^{\gamma\beta}}{\mathbf{I}_e^{\alpha\gamma} \mathbf{I}_e^{\gamma\beta} (\gamma_k \gamma_l)^{1/2}} \\ \mu_{(k,l,m)}^{(3)} &= \left( \frac{\partial^3 \mu}{\partial Q_k \partial Q_l \partial Q_m} \right)_e = - \frac{1}{2} \mathbf{I}_e^{-1} \mathbf{a} \mathbf{I}_e^{-1} \mathbf{a} \mathbf{I}_e^{-1} \mathbf{a} \mathbf{I}_e^{-1} \Rightarrow \mu_{(k,l,m)}^{(3)\alpha\beta} = \left( \frac{\partial^3 \mu_{\alpha\beta}}{\partial Q_k \partial Q_l \partial Q_m} \right)_e \\ &= - \frac{1}{2} \sum_{\gamma\delta} \left[ \frac{a_k^{\alpha\gamma} a_l^{\gamma\delta} a_m^{\delta\beta} + a_k^{\alpha\gamma} a_m^{\gamma\delta} a_l^{\delta\beta} + a_m^{\alpha\gamma} a_l^{\gamma\delta} a_k^{\delta\beta} + a_l^{\alpha\gamma} a_k^{\gamma\delta} a_m^{\delta\beta} + a_m^{\alpha\gamma} a_k^{\gamma\delta} a_l^{\delta\beta} + a_l^{\alpha\gamma} a_m^{\gamma\delta} a_k^{\delta\beta}}{\mathbf{I}_e^{\alpha\gamma} \mathbf{I}_e^{\gamma\delta} \mathbf{I}_e^{\delta\beta} (\gamma_k \gamma_l \gamma_m)^{1/2}} \right] \\ &\quad \cdot \quad \cdot \quad \cdot \\ &\quad \cdot \quad \cdot \quad \cdot \\ &\quad \cdot \quad \cdot \quad \cdot\end{aligned}\quad (15)$$

The first step in the quasi-analytic evaluation of the kinetic energy is the calculation of the set of derivatives of  $\mu_{\alpha\beta}$ . Fortunately, this is

**Quasi-Analytic Integration of  $\hat{K}(q, \hat{p})$ .** The KEO beyond the harmonic contribution, i.e.,  $\hat{K}_{\text{nonlinear}}(q, \hat{p})$  and  $\hat{K}_{\text{linear}}(q, \hat{p})$ , is defined in eqs 7 and 8 for nonlinear and linear configurations, respectively. These equations are a function of  $\mu$ , the reciprocal of  $\mathbf{I}$ , which is quadratic in the rectilinear normal coordinates, see eqs 3 and 6. However  $\mathbf{I}$  can also be written as a product of three terms, two of them linear in the rectilinear normal coordinate  $(q)$ ,<sup>70</sup> and for which Watson proposed the following general formulation:

$$\mu = \mathbf{I}_e^{-1/2} \left( 1 + \frac{1}{2} \mathbf{b} \right)^{-2} \mathbf{I}_e^{-1/2} \quad \text{with} \quad \mathbf{b} \equiv \sum_k \mathbf{I}_e^{-1/2} \mathbf{a}_k \mathbf{I}_e^{-1/2} \gamma_k^{-1/2} q_k \quad (11)$$

with the elements of  $\mathbf{a}_k$  defined via eq 4. With the expansion of the binomial  $(1 + 1/2\mathbf{b})^{-2}$ ,<sup>99</sup> the expression of  $\mu_{\alpha\beta}$  derived earlier by Amat and Henry<sup>95,96</sup> is now reformulated as follows:

$$\begin{aligned}\mu &= \mathbf{I}_e^{-1/2} \left\{ 1 - \mathbf{b} + \frac{3}{4} \mathbf{b}^2 - \frac{1}{2} \mathbf{b}^3 + \dots \right\} \mathbf{I}_e^{-1/2} \\ &= \mathbf{I}_e^{-1} - \mathbf{I}_e^{-1} \mathbf{a} \mathbf{I}_e^{-1} + \frac{3}{4} \mathbf{I}_e^{-1} \mathbf{a} \mathbf{I}_e^{-1} \mathbf{a} \mathbf{I}_e^{-1} - \frac{1}{2} \mathbf{I}_e^{-1} \mathbf{a} \mathbf{I}_e^{-1} \mathbf{a} \mathbf{I}_e^{-1} \mathbf{a} \mathbf{I}_e^{-1} + \dots\end{aligned}\quad (12)$$

where

$$\mathbf{a} = \sum_{k=1}^{3N-6(5)} \mathbf{a}_k \gamma_k^{-1/2} q_k \quad (13)$$

For semirigid molecules, vibrations are small amplitude motions, and this allows the components of the reciprocal modified moment of inertia,  $\mu_{\alpha\beta}$ , to be represented by a Taylor expansion with respect to the rectilinear normal coordinates,<sup>100</sup> viz.:

$$\begin{aligned}\mu_{\alpha\beta} &= \mu_e^{\alpha\beta} \delta_{\alpha\beta} + \sum_k \mu_{(k)}^{(1)\alpha\beta} q_k + \frac{1}{2} \sum_{kl} \mu_{(k,l)}^{(2)\alpha\beta} q_k q_l \\ &+ \frac{1}{6} \sum_{klm} \mu_{(k,l,m)}^{(3)\alpha\beta} q_k q_l q_m + \frac{1}{24} \sum_{klmn} \mu_{(k,l,m,n)}^{(4)\alpha\beta} q_k q_l q_m q_n + \dots\end{aligned}\quad (14)$$

and  $\mu_e^{\alpha\beta}$  is defined by  $\mu_e^{\alpha\beta} = \delta_{\alpha\beta} (\mathbf{I}_e^{-1})^{\alpha\beta}$ . In the reduced dimensionless normal-coordinate representation derivatives of  $\mu_{\alpha\beta}$  to all orders [ $\mu_{(k)}^{(1)\alpha\beta}$ ,  $\mu_{(k,l)}^{(2)\alpha\beta}$ ,  $\mu_{(k,l,m)}^{(3)\alpha\beta}$ , ...] can be associated with the terms of eq 12 and expressed entirely in terms of the first derivatives of the inertia tensor with respect to the rectilinear normal coordinates, i.e.:

easily affordable as only products of  $a_k^{\alpha\beta}$  are involved, i.e., derivatives of the  $\alpha\beta$ -component of the inertia tensor,  $I_{\alpha\beta}$ , with respect to the

rectilinear normal coordinate  $Q_k$ , see eq 4. Although the evaluation of integrals involving the coordinate and momentum operators is a trivial matter,<sup>98</sup> the processing and bookkeeping associated with sorting and linking these integrals and these contributions to the Hamiltonian is the most complicated and tedious element of the present approach particularly in the case of the Coriolis term.<sup>101</sup> When this difficulty is overcome, an accurate and efficient computation of the kinetic energy can be achieved.

The complexity associated with computing  $\hat{K}(q, \hat{p})$  can be reduced by a formulation in terms of ladder operators. Initial work in this direction was carried out for nonlinear triatomic systems by Huber<sup>102</sup> and continued and extended by others in the context of variational and perturbational approaches.<sup>6,7,83,103</sup> Details of the ladder operator formalism are described in the next section.

**Ladder Operator Formalism.** Normalized raising,  $\mathcal{L}_k^+$ , and lowering,  $\mathcal{L}_k^-$ , operators for the vibrational normal mode  $k$  can be defined as

$$\mathcal{L}_k^+ = \mathcal{N}(-i\hat{p}_k + q_k); \quad \mathcal{L}_k^- = \mathcal{N}(i\hat{p}_k + q_k) \quad (16)$$

The two ladder operators,  $\mathcal{L}_k^+$  and  $\mathcal{L}_k^-$ , act only on the part of the total vibrational wave function,  $\Psi = \phi_{n_1}(q_1)\phi_{n_2}(q_2)\phi_{n_k}(q_k) \dots = |n_1, n_2, \dots, n_k, \dots\rangle$ , which depends on the  $k$ -th rectilinear normal coordinate, i.e.,  $\phi_{n_k}(q_k) = |n_k\rangle$ . The normalization constant is chosen in such a way that:

$$\begin{aligned} \mathcal{L}_k^+ | \dots, n_k, \dots \rangle &= \left( \frac{n_k + 1}{2} \right)^{1/2} | \dots, n_k + 1, \dots \rangle \\ \mathcal{L}_k^- | \dots, n_k, \dots \rangle &= \left( \frac{n_k}{2} \right)^{1/2} | \dots, n_k - 1, \dots \rangle \end{aligned} \quad (17)$$

The vibrational quantum number associated with normal mode  $k$  is represented by  $n_k$ . Solving eqs 16 for  $\hat{p}_k$  and  $q_k$  yields

$$q_k = (\mathcal{L}_k^+ + \mathcal{L}_k^-); \quad \hat{p}_k = i(\mathcal{L}_k^+ - \mathcal{L}_k^-) \quad (18)$$

Using eq 18, the terms of the operator  $\hat{K}(q, \hat{p})$  can be written in a ladder operator formalism. The components of the modified reciprocal moment of inertia are functions of the rectilinear normal coordinates and are thus also easily expressed in terms of ladder operators as

$$\begin{aligned} \mu_{\alpha\beta} &= I_e^{-1} + \sum_k \mu_{(k)}^{(1)\alpha\beta} (\mathcal{L}_k^+ + \mathcal{L}_k^-) \\ &+ \frac{1}{2} \sum_{kl} \mu_{(k,l)}^{(2)\alpha\beta} (\mathcal{L}_k^+ + \mathcal{L}_k^-) (\mathcal{L}_l^+ + \mathcal{L}_l^-) \\ &+ \frac{1}{6} \sum_{klm} \mu_{(k,l,m)}^{(3)\alpha\beta} (\mathcal{L}_k^+ + \mathcal{L}_k^-) (\mathcal{L}_l^+ + \mathcal{L}_l^-) (\mathcal{L}_m^+ + \mathcal{L}_m^-) \\ &+ \frac{1}{24} \sum_{klmn} \mu_{(k,l,m,n)}^{(4)\alpha\beta} (\mathcal{L}_k^+ + \mathcal{L}_k^-) (\mathcal{L}_l^+ + \mathcal{L}_l^-) (\mathcal{L}_m^+ + \mathcal{L}_m^-) \\ &\quad (\mathcal{L}_n^+ + \mathcal{L}_n^-) + \dots \end{aligned} \quad (19)$$

The effective vibrational angular momentum  $\hat{\pi}_\alpha$  defined in eq 2 involves the product  $q_k \hat{p}_k$  and has a more complicated structure.<sup>102</sup> This operator is given by

$$\begin{aligned} \hat{\pi}_\alpha &= i \sum_{k < l} \xi_{kl}^\alpha [\mathbf{R}_{-}^{kl} (\mathcal{L}_k^+ \mathcal{L}_l^+ - \mathcal{L}_k^- \mathcal{L}_l^-) \\ &+ \mathbf{R}_{+}^{kl} (\mathcal{L}_k^- \mathcal{L}_l^+ - \mathcal{L}_k^+ \mathcal{L}_l^-)] \end{aligned} \quad (20)$$

where the coefficients  $\mathbf{R}_{-}^{kl}$  and  $\mathbf{R}_{+}^{kl}$  are defined by

$$\begin{aligned} \mathbf{R}_{-}^{kl} &= \left( \frac{\omega_l}{\omega_k} \right)^{1/2} - \left( \frac{\omega_k}{\omega_l} \right)^{1/2}; \\ \mathbf{R}_{+}^{kl} &= \left( \frac{\omega_l}{\omega_k} \right)^{1/2} + \left( \frac{\omega_k}{\omega_l} \right)^{1/2} \end{aligned} \quad (21)$$

Based on the Taylor expansion of  $\mu_{\alpha\beta}$ , the Watson term for nonlinear configurations ( $\hat{U}(q)$ ) and the vibrational Coriolis term ( $\hat{C}(q, \hat{p})$ ) for both linear and nonlinear systems can be written in terms of a hierarchy of contributions or “orders” as follows:

$$\begin{aligned} \hat{O} &= \sum_{i=0}^{\infty} \hat{O}^{(i)} \\ &= \hat{O}^{(0)} + \hat{O}^{(1)} + \hat{O}^{(2)} + \hat{O}^{(3)} + \hat{O}^{(4)} + \dots \end{aligned} \quad (22)$$

where  $\hat{O} = \hat{U}(q), \hat{C}(q, \hat{p})$  and  $\hat{O}^{(i)} = \hat{U}^{(i)}(q), \hat{C}^{(i)}(q, \hat{p})$ .

For  $\hat{U}$  the specific terms in the expansion are:

$$\begin{aligned} \hat{U}^{(0)} &= -\frac{\hbar^2}{8} I_e^{-1} \\ \hat{U}^{(1)} &= -\frac{\hbar^2}{8} \sum_k \mu_{(k)}^{(1)\alpha\alpha} (\mathcal{L}_k^+ + \mathcal{L}_k^-) \\ \hat{U}^{(2)} &= -\frac{\hbar^2}{16} \sum_{kl} \mu_{(k,l)}^{(2)\alpha\alpha} (\mathcal{L}_k^+ \mathcal{L}_l^+ + \mathcal{L}_k^+ \mathcal{L}_l^- + \mathcal{L}_k^- \mathcal{L}_l^+ + \mathcal{L}_k^- \mathcal{L}_l^-) \\ \hat{U}^{(3)} &= -\frac{\hbar^2}{48} \sum_{klm} \mu_{(k,l,m)}^{(3)\alpha\alpha} (\mathcal{L}_k^+ \mathcal{L}_l^+ \mathcal{L}_m^+ + \mathcal{L}_k^+ \mathcal{L}_l^+ \mathcal{L}_m^- + \mathcal{L}_k^+ \mathcal{L}_l^- \mathcal{L}_m^+ + \mathcal{L}_k^+ \mathcal{L}_l^- \mathcal{L}_m^- \\ &\quad + \mathcal{L}_k^- \mathcal{L}_l^+ \mathcal{L}_m^+ + \mathcal{L}_k^- \mathcal{L}_l^+ \mathcal{L}_m^- + \mathcal{L}_k^- \mathcal{L}_l^- \mathcal{L}_m^+ + \mathcal{L}_k^- \mathcal{L}_l^- \mathcal{L}_m^-) \\ &\quad \vdots \quad \vdots \quad \vdots \end{aligned} \quad (23)$$

Considering the commutation relation between  $\hat{\pi}_\alpha$  and  $\mu$ , i.e.,  $\Sigma_\alpha [\hat{\pi}_\alpha \mu_{\alpha\beta}] = 0$ , terms in the expansion of the Coriolis term,  $\hat{C}(q, \hat{p})$ , (eqs 7, 8, and 22) take the following general form:

$$\begin{aligned} \hat{C}^{(0)} &= -\sum_{r < s} \sum_{t < u} \sum_{\alpha\beta} B_{rs}^{\alpha} \xi_{rs}^{\alpha\beta} \zeta_{tu}^{\beta} (\mathbf{R}_{-}^{\alpha} \mathbf{R}_{-}^{\beta} \hat{C}_{a,(rstu)}^{(0)} + \mathbf{R}_{rs}^{\alpha} \mathbf{R}_{tu}^{\beta} \hat{C}_{b,(rstu)}^{(0)} \\ &\quad + \mathbf{R}_{rs}^{\alpha} \mathbf{R}_{tu}^{\beta} \hat{C}_{c,(rstu)}^{(0)} + \mathbf{R}_{rs}^{\alpha} \mathbf{R}_{tu}^{\beta} \hat{C}_{d,(rstu)}^{(0)}) \\ \hat{C}^{(1)} &= -\sum_{r < s < t < u} \sum_{\alpha\beta} \mu_{(k)}^{(1)\alpha\beta} \xi_{rs}^{\alpha} \zeta_{tu}^{\beta} (\mathbf{R}_{-}^{\alpha} \mathbf{R}_{-}^{\beta} \hat{C}_{a,(k;rstu)}^{(1)} + \mathbf{R}_{rs}^{\alpha} \mathbf{R}_{tu}^{\beta} \hat{C}_{b,(k;rstu)}^{(1)} \\ &\quad + \mathbf{R}_{rs}^{\alpha} \mathbf{R}_{tu}^{\beta} \hat{C}_{c,(k;rstu)}^{(1)} + \mathbf{R}_{rs}^{\alpha} \mathbf{R}_{tu}^{\beta} \hat{C}_{d,(k;rstu)}^{(1)}) \\ \hat{C}^{(2)} &= -\sum_{r < s < t < u} \sum_{\alpha\beta} \mu_{(k,l)}^{(2)\alpha\beta} \xi_{rs}^{\alpha} \zeta_{tu}^{\beta} (\mathbf{R}_{-}^{\alpha} \mathbf{R}_{-}^{\beta} \hat{C}_{a,(kl;rstu)}^{(2)} + \mathbf{R}_{rs}^{\alpha} \mathbf{R}_{tu}^{\beta} \hat{C}_{b,(kl;rstu)}^{(2)} \\ &\quad + \mathbf{R}_{rs}^{\alpha} \mathbf{R}_{tu}^{\beta} \hat{C}_{c,(kl;rstu)}^{(2)} + \mathbf{R}_{rs}^{\alpha} \mathbf{R}_{tu}^{\beta} \hat{C}_{d,(kl;rstu)}^{(2)}) \dots \end{aligned} \quad (24)$$

The operators  $\hat{C}_a^{(i)}$ ,  $\hat{C}_b^{(i)}$ ,  $\hat{C}_c^{(i)}$ , and  $\hat{C}_d^{(i)}$  ( $i = 0, 1, 2, \dots, \infty$ ) represent sums of products of ladder operators. Explicit expressions for the two first sets of the series are given next:

$i = 0$

$$\begin{aligned} \hat{C}_{a,(rstu)}^{(0)} &= \mathcal{L}_r^+ \mathcal{L}_s^+ \mathcal{L}_t^+ \mathcal{L}_u^+ - \mathcal{L}_r^+ \mathcal{L}_s^+ \mathcal{L}_t^- \mathcal{L}_u^- \\ &\quad - \mathcal{L}_r^- \mathcal{L}_s^- \mathcal{L}_t^+ \mathcal{L}_u^+ + \mathcal{L}_r^- \mathcal{L}_s^- \mathcal{L}_t^- \mathcal{L}_u^- \\ \hat{C}_{b,(rstu)}^{(0)} &= \mathcal{L}_r^+ \mathcal{L}_s^+ \mathcal{L}_t^- \mathcal{L}_u^+ - \mathcal{L}_r^+ \mathcal{L}_s^+ \mathcal{L}_t^+ \mathcal{L}_u^- \\ &\quad - \mathcal{L}_r^- \mathcal{L}_s^- \mathcal{L}_t^- \mathcal{L}_u^+ + \mathcal{L}_r^- \mathcal{L}_s^- \mathcal{L}_t^+ \mathcal{L}_u^- \\ \hat{C}_{c,(rstu)}^{(0)} &= \mathcal{L}_r^- \mathcal{L}_s^+ \mathcal{L}_t^+ \mathcal{L}_u^+ - \mathcal{L}_r^- \mathcal{L}_s^+ \mathcal{L}_t^- \mathcal{L}_u^- \\ &\quad - \mathcal{L}_r^+ \mathcal{L}_s^- \mathcal{L}_t^+ \mathcal{L}_u^+ + \mathcal{L}_r^+ \mathcal{L}_s^- \mathcal{L}_t^- \mathcal{L}_u^- \\ \hat{C}_{d,(rstu)}^{(0)} &= \mathcal{L}_r^- \mathcal{L}_s^+ \mathcal{L}_t^- \mathcal{L}_u^+ - \mathcal{L}_r^- \mathcal{L}_s^+ \mathcal{L}_t^+ \mathcal{L}_u^- \\ &\quad - \mathcal{L}_r^+ \mathcal{L}_s^- \mathcal{L}_t^- \mathcal{L}_u^+ + \mathcal{L}_r^+ \mathcal{L}_s^- \mathcal{L}_t^+ \mathcal{L}_u^- \end{aligned} \quad (25)$$



$i = 1$

$$\begin{aligned}
 \hat{C}_{a_j(k;rstu)}^{(1)} &= \mathcal{L}_k^+ \mathcal{L}_r^+ \mathcal{L}_s^+ \mathcal{L}_t^+ \mathcal{L}_u^+ - \mathcal{L}_k^+ \mathcal{L}_r^+ \mathcal{L}_s^+ \mathcal{L}_t^- \mathcal{L}_u^- \\
 &\quad - \mathcal{L}_k^+ \mathcal{L}_r^- \mathcal{L}_s^- \mathcal{L}_t^+ \mathcal{L}_u^+ + \mathcal{L}_k^+ \mathcal{L}_r^- \mathcal{L}_s^- \mathcal{L}_t^- \mathcal{L}_u^- \\
 &\quad + \mathcal{L}_k^- \mathcal{L}_r^+ \mathcal{L}_s^+ \mathcal{L}_t^+ \mathcal{L}_u^+ - \mathcal{L}_k^- \mathcal{L}_r^+ \mathcal{L}_s^+ \mathcal{L}_t^- \mathcal{L}_u^- \\
 &\quad - \mathcal{L}_k^- \mathcal{L}_r^- \mathcal{L}_s^- \mathcal{L}_t^+ \mathcal{L}_u^+ + \mathcal{L}_k^- \mathcal{L}_r^- \mathcal{L}_s^- \mathcal{L}_t^- \mathcal{L}_u^- \\
 \hat{C}_{b_j(k;rstu)}^{(1)} &= \mathcal{L}_k^+ \mathcal{L}_r^+ \mathcal{L}_s^+ \mathcal{L}_t^- \mathcal{L}_u^- - \mathcal{L}_k^+ \mathcal{L}_r^+ \mathcal{L}_s^- \mathcal{L}_t^+ \mathcal{L}_u^+ \\
 &\quad - \mathcal{L}_k^+ \mathcal{L}_r^- \mathcal{L}_s^- \mathcal{L}_t^+ \mathcal{L}_u^+ + \mathcal{L}_k^+ \mathcal{L}_r^- \mathcal{L}_s^- \mathcal{L}_t^- \mathcal{L}_u^- \\
 &\quad + \mathcal{L}_k^- \mathcal{L}_r^+ \mathcal{L}_s^+ \mathcal{L}_t^+ \mathcal{L}_u^+ - \mathcal{L}_k^- \mathcal{L}_r^+ \mathcal{L}_s^+ \mathcal{L}_t^- \mathcal{L}_u^- \\
 &\quad - \mathcal{L}_k^- \mathcal{L}_r^- \mathcal{L}_s^- \mathcal{L}_t^+ \mathcal{L}_u^+ + \mathcal{L}_k^- \mathcal{L}_r^- \mathcal{L}_s^- \mathcal{L}_t^- \mathcal{L}_u^- \\
 \hat{C}_{c_j(k;rstu)}^{(1)} &= \mathcal{L}_k^+ \mathcal{L}_r^+ \mathcal{L}_s^+ \mathcal{L}_t^+ \mathcal{L}_u^+ - \mathcal{L}_k^+ \mathcal{L}_r^+ \mathcal{L}_s^+ \mathcal{L}_t^- \mathcal{L}_u^- \\
 &\quad - \mathcal{L}_k^+ \mathcal{L}_r^+ \mathcal{L}_s^- \mathcal{L}_t^+ \mathcal{L}_u^+ + \mathcal{L}_k^+ \mathcal{L}_r^+ \mathcal{L}_s^- \mathcal{L}_t^- \mathcal{L}_u^- \\
 &\quad + \mathcal{L}_k^- \mathcal{L}_r^- \mathcal{L}_s^- \mathcal{L}_t^+ \mathcal{L}_u^+ - \mathcal{L}_k^- \mathcal{L}_r^- \mathcal{L}_s^- \mathcal{L}_t^- \mathcal{L}_u^- \\
 &\quad - \mathcal{L}_k^- \mathcal{L}_r^- \mathcal{L}_s^+ \mathcal{L}_t^+ \mathcal{L}_u^+ + \mathcal{L}_k^- \mathcal{L}_r^- \mathcal{L}_s^+ \mathcal{L}_t^- \mathcal{L}_u^- \\
 \hat{C}_{d_j(k;rstu)}^{(1)} &= \mathcal{L}_k^+ \mathcal{L}_r^+ \mathcal{L}_s^+ \mathcal{L}_t^- \mathcal{L}_u^- - \mathcal{L}_k^+ \mathcal{L}_r^+ \mathcal{L}_s^- \mathcal{L}_t^+ \mathcal{L}_u^+ \\
 &\quad - \mathcal{L}_k^+ \mathcal{L}_r^- \mathcal{L}_s^- \mathcal{L}_t^+ \mathcal{L}_u^+ + \mathcal{L}_k^+ \mathcal{L}_r^- \mathcal{L}_s^- \mathcal{L}_t^- \mathcal{L}_u^- \\
 &\quad + \mathcal{L}_k^- \mathcal{L}_r^+ \mathcal{L}_s^+ \mathcal{L}_t^+ \mathcal{L}_u^+ - \mathcal{L}_k^- \mathcal{L}_r^+ \mathcal{L}_s^+ \mathcal{L}_t^- \mathcal{L}_u^- \\
 &\quad - \mathcal{L}_k^- \mathcal{L}_r^- \mathcal{L}_s^- \mathcal{L}_t^+ \mathcal{L}_u^+ + \mathcal{L}_k^- \mathcal{L}_r^- \mathcal{L}_s^- \mathcal{L}_t^- \mathcal{L}_u^- \quad (26)
 \end{aligned}$$

## IMPLEMENTATION

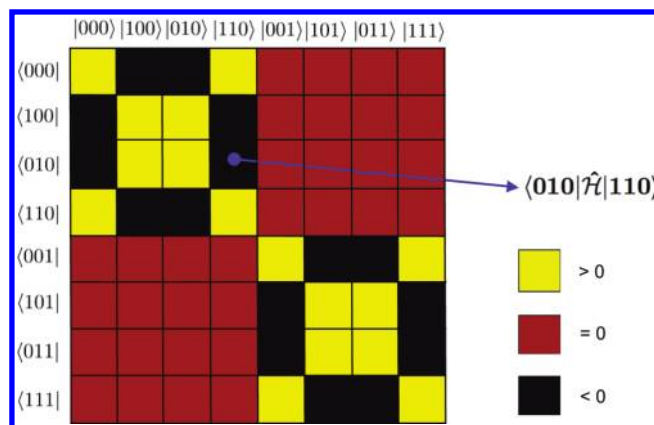
The implementation follows the algebraic expressions outlined here and keeps the number of basis functions per degree of freedom independent from the number of sampling points used for the quadrature grid. Three main features characterize the present implementation: (a) determination of the prefactors resulting from the expansion of the modified reciprocal moment of inertia tensor,  $\mu$ ; (b) evaluation of the associated integrals (matrix elements); and (c) the procedure used to obtain eigenvalues of the Hamiltonian matrix. These are discussed in the following paragraphs.

First, the prefactors in eqs 14 and 19 are calculated by an efficient permutation matrix multiplication algorithm where it is essential to use loop unrolling as well as to make full use of restricted summations. Regarding the second point, the integrals depend only on a sum of ladder operator products (see, for example eqs 25 and 26). These integrals are represented by lists of integers where 1 and 0 identify raising and lowering operators, respectively. The latter lists are regrouped by normal modes and written as a string of bits. Each string can be processed in a recursive scheme. By systematically applying the commutation relations

$$[\mathcal{L}_i^+, \mathcal{L}_j^+]_- = 0; \quad [\mathcal{L}_i^-, \mathcal{L}_j^-]_- = 0; \quad [\mathcal{L}_i^-, \mathcal{L}_j^+]_- = \delta_{ij} \quad (27)$$

where  $i, j, \dots$  represent normal modes or vibrational degrees of freedom, and following Wick's theorem for bosons,<sup>104</sup> the raising operators can be clustered on the left (normal ordering) or the right (antinormal ordering).<sup>105</sup> For example, in the case of the sum products of three ladder operators associated with the vibrational mode  $i$ , an antinormal ordering leads the next results:

$$\begin{aligned}
 &\mathcal{L}_i^+ \mathcal{L}_i^+ \mathcal{L}_i^+ + \mathcal{L}_i^- \mathcal{L}_i^+ \mathcal{L}_i^+ + \mathcal{L}_i^+ \mathcal{L}_i^- \mathcal{L}_i^+ + \mathcal{L}_i^+ \mathcal{L}_i^+ \mathcal{L}_i^- + \mathcal{L}_i^- \mathcal{L}_i^+ \mathcal{L}_i^- \\
 &\quad + \mathcal{L}_i^- \mathcal{L}_i^+ \mathcal{L}_i^+ + \mathcal{L}_i^+ \mathcal{L}_i^- \mathcal{L}_i^- + \mathcal{L}_i^- \mathcal{L}_i^- \mathcal{L}_i^+ \\
 &= 2(\mathcal{L}_i^- \mathcal{L}_i^+ \mathcal{L}_i^+ + \mathcal{L}_i^- \mathcal{L}_i^- \mathcal{L}_i^+) - 3(\mathcal{L}_i^+ + \mathcal{L}_i^-) \quad (28)
 \end{aligned}$$



**Figure 1.** Schematic structure of the Hamiltonian matrix,  $H$ , for a  $XY_2$  molecule ( $C_{2v}$  symmetry) in the FBR including only the anharmonic potential energy and harmonic oscillator, i.e.,  $\hat{\mathcal{H}}_0 + \hat{V}_{\text{anh}}$ . (Two basis functions were used per vibrational degree of freedom).

According to the relations above, the eight possible sequences of three lowering and raising operators are reduced to four combinations of three operators, a contribution from  $\mathcal{L}_i^-$  and another from  $\mathcal{L}_i^+$ . Within this framework, and for a given order  $n$  (see Section II), the number of integrals involving a product of  $n$  operators,  $[n(n-1)+2]$ , is reduced by expressing them in terms of normal- or antinormal-ordered products of  $n, n-2, n-4, n-6, \dots, p$  operators, where  $p = 1$  or  $0$  for  $n$  odd or even, respectively. In the present work we have chosen an antinormal ordering, but we note that the choice of normal or antinormal ordering is arbitrary.<sup>106</sup>

For an odd order  $n$ , all contributions of antinormal products of  $n, n-2, n-4, \dots, 1$  operators associated with a vibrational mode  $i$ ,  $\Omega_{\text{odd},i}$  are obtained by the expression:

$$\begin{aligned}
 \Omega_{\text{odd},i} &\Rightarrow \sum_{l=0}^n \binom{n}{l} (\mathcal{L}_i^-)^l (\mathcal{L}_i^+)^{n-l} \\
 &\quad + \sum_{m=1}^{(n-1)/2} \left\{ \Theta_m (\mathcal{L}_i^-)^l (\mathcal{L}_i^+)^{n-2m-l} \right\} \quad (29)
 \end{aligned}$$

and in the case of an even order  $n$ ,  $\Omega_{\text{even},i}$  the corresponding expression is

$$\begin{aligned}
 \Omega_{\text{even},i} &\Rightarrow \sum_{l=0}^n \binom{n}{l} (\mathcal{L}_i^-)^l (\mathcal{L}_i^+)^{n-l} \\
 &\quad + \sum_{m=1}^{(n-2)/2} \left\{ \Theta_m (\mathcal{L}_i^-)^l (\mathcal{L}_i^+)^{n-2m-l} \right\} + (-1)^{r+n} (n-1)!! \quad (30)
 \end{aligned}$$

where

$$\Theta_m = \frac{(-1)^m}{m! 2^m} \left[ \prod_{k=1}^m \frac{(n-2k+2)!}{(n-2k)!} \right] \left[ \sum_{l=0}^{n-2m} n-2m \binom{n-2m}{l} \right] \quad (31)$$

and

$r = 1$  for  $n = 2, 6, 10, 14, \dots$

and  $r = 0$  for  $n = 4, 8, 12, 16, \dots$

Thus, the  $n(n - 1) + 2$  combinations of products of  $n$  raising ( $\mathcal{L}_i^+$ ) and lowering ( $\mathcal{L}_i^-$ ) operators that appear at  $n$ -th order can be reduced to only  $(n + 1)$  combinations of products of  $n$  operators,  $(n - 1)$  products of  $(n - 2)$  operators,  $(n - 3)$  products of  $(n - 4)$  operators, etc. In

$$\begin{aligned}
 \mathcal{L}_i^- (\mathcal{L}_i^-)^l (\mathcal{L}_i^+)^{n-l} &= (\mathcal{L}_i^-)^{l+1} (\mathcal{L}_i^+)^{n-l} \\
 \mathcal{L}_i^+ (\mathcal{L}_i^-)^l (\mathcal{L}_i^+)^{n-l} &= (\mathcal{L}_i^-)^l (\mathcal{L}_i^+)^{n-l+1} - l (\mathcal{L}_i^-)^{l-1} (\mathcal{L}_i^+)^{n-l} \\
 \mathcal{L}_i^- \mathcal{L}_i^- (\mathcal{L}_i^-)^l (\mathcal{L}_i^+)^{n-l} &= (\mathcal{L}_i^-)^{l+2} (\mathcal{L}_i^+)^{n-l} \\
 \mathcal{L}_i^- \mathcal{L}_i^+ (\mathcal{L}_i^-)^l (\mathcal{L}_i^+)^{n-l} &= (\mathcal{L}_i^-)^{l+1} (\mathcal{L}_i^+)^{n-l+1} - l (\mathcal{L}_i^-)^l (\mathcal{L}_i^+)^{n-l} \\
 \mathcal{L}_i^+ \mathcal{L}_i^- (\mathcal{L}_i^-)^l (\mathcal{L}_i^+)^{n-l} &= (\mathcal{L}_i^-)^{l+1} (\mathcal{L}_i^+)^{n-l+1} - (l+1) (\mathcal{L}_i^-)^l (\mathcal{L}_i^+)^{n-l} \\
 \mathcal{L}_i^+ \mathcal{L}_i^+ (\mathcal{L}_i^-)^l (\mathcal{L}_i^+)^{n-l} &= (\mathcal{L}_i^-)^l (\mathcal{L}_i^+)^{n-l+2} - 2l (\mathcal{L}_i^-)^{l-1} (\mathcal{L}_i^+)^{n-l+1} + l(l-1) (\mathcal{L}_i^-)^{l-2} (\mathcal{L}_i^+)^{n-l}
 \end{aligned} \quad (32)$$

where  $l$  is an integer and its values ranges over the interval  $1 \leq l \leq n - 1$ . This scheme allows the analytic solution of integrals involving an arbitrary number of ladder operators. This kernel for evaluating the Hamiltonian matrix elements resulting from the  $\hat{K}(q, \hat{p})$  operator was checked by implementing the lower-order Hamiltonian contributions explicitly in terms of dimensionless rectilinear normal coordinates ( $q$ ) and its conjugate momentum ( $\hat{p}$ ).

Finally, concerning the diagonalization procedure, a few remarks should be made in relation to the structure of the Hamiltonian matrix,  $\mathbf{H} = \langle \Psi | \hat{\mathcal{H}} | \Psi \rangle$ . In FBR the matrix elements of  $\mathbf{H}$  can be schematically represented by distinguishing positive, negative and zero values (Figures 1 and 2). In particular, Figure 1 illustrates the structure of  $\mathbf{H}$  for a  $\text{XY}_2$  molecule ( $C_{2v}$  symmetry) using two basis functions per degree of freedom and ordering the vibrational modes by increasing value of their harmonic frequency, i.e., first the two totally symmetric vibrations ( $a_1$  symmetry) and next the asymmetric stretching mode ( $b_2$  symmetry). Only the harmonic oscillator operator and the anharmonic potential were included as part of  $\hat{\mathcal{H}}$ , i.e.,  $\hat{\mathcal{H}}_0 + \hat{V}_{\text{anh}}(q)$ . The matrix is block diagonal due to symmetry constraints, all diagonal contributions are positive, and about half of the elements have values larger than  $1 \text{ cm}^{-1}$ . Increasing the number of basis functions per vibrational degree of freedom preserves the block diagonal profile but obviously increases the density of nonzero matrix elements (see first column of Figure 2). The structure of  $\mathbf{H}$  due to the contributions from different orders of the pseudopotential term ( $\hat{U}$ ) is presented in Figure SI of the Supporting Information. As in the case of  $\hat{V}(q)$ ,  $\hat{U}$  is a function of the coordinate operator, and consequently the structure of the contributions to  $\mathbf{H}$  is similar to that of  $\langle \Psi | \hat{V}_{\text{harm}} + \hat{V}_{\text{anh}} | \Psi \rangle$  (second column of Figure 2,<sup>107</sup> with the proviso that at zeroth-order ( $\hat{U}^{(0)}$ ) only about 1% of them have a value larger than  $1 \text{ cm}^{-1}$  and at tenth-order ( $\hat{U}^{(10)}$ ) no contribution is larger than  $1 \text{ cm}^{-1}$  and only 2% of them have values larger than  $10^{-2} \text{ cm}^{-1}$ . The nonzero contributions to  $\mathbf{H}$  resulting from the vibrational Coriolis term,  $\hat{C}$ , have a more peculiar structure, in the present example, mostly because of symmetry considerations,<sup>108</sup> (Figure SII, Supporting Information and third column of Figure 2). Nevertheless, at zeroth-order ( $\hat{C}^{(0)}$ ) only 5% of these contributions have values larger than  $1 \text{ cm}^{-1}$ , while at tenth-order ( $\hat{C}^{(10)}$ ) there are no elements larger than  $1 \text{ cm}^{-1}$  and only 2% of them are larger than  $10^{-5} \text{ cm}^{-1}$ . For Coriolis and pseudopotential contributions, the number of nonzero matrix elements increases rapidly with order, see Figure SIII of the Supporting Information. The complete structure of the Hamiltonian matrix, including all terms, is illustrated in the last column

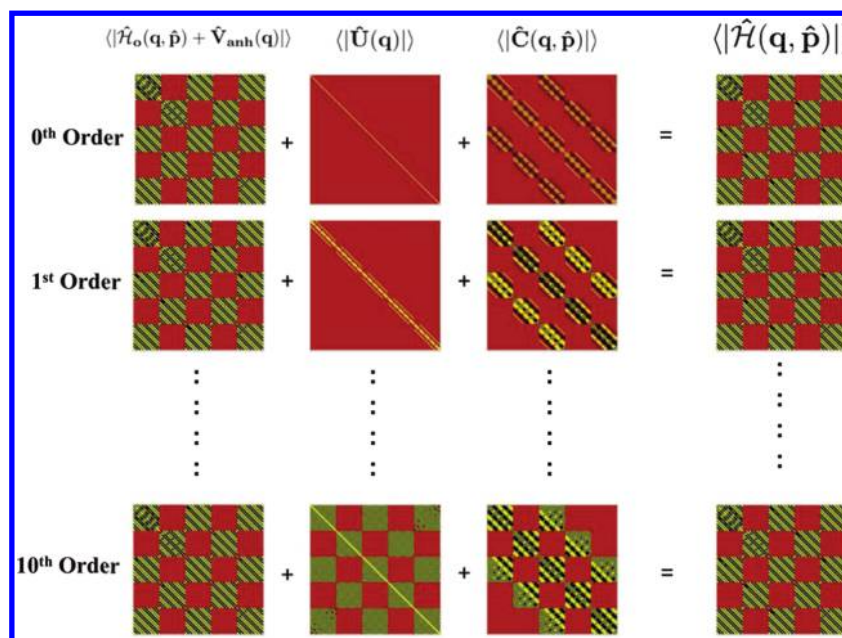
order to maintain the antinormal ordering and exploit eqs 29–31 computing the vibrational Coriolis term, the following relations were taken into account for a particular vibration  $i$  and for each order of the expansions defined by eqs 22 and 24:

of Figure 2. The sequence of orders in this Figure shows a dense  $\mathbf{H}$ , which is characterized by two aspects. First, the contribution from the potential energy quantitatively dominates the rest, and second the scarcity of zero matrix elements becomes larger with the increase of basis functions per degree of freedom and with the increase of order in the  $\hat{U}$  and  $\hat{C}$  contributions. These characteristics had to be considered in the implementation.

For triatomic molecules the eigenvalue problem is solved by direct diagonalization of  $\mathbf{H}$ , however for larger systems, a complete or partial diagonalization is prohibitively expensive (even if the Hamiltonian matrix still can be kept in main memory), and an iterative Lanczos procedure<sup>109,110</sup> is applied. Here, the key step is the multiplication of the Hamiltonian matrix with the Lanczos vector,  $\mathbf{V}_L$ :  $\mathbf{H}$  does not need to be constructed and stored explicitly, and only its product with  $\mathbf{V}_L$  is required. In order to construct the resulting product–vector,  $\mathbf{V}_T$ , a process of sequential additions of the different contributions from the Hamiltonian matrix is performed, i.e., first the harmonic oscillator energies are multiplied with the trial vector and added to  $\mathbf{V}_T$ . This is followed by an efficient contraction of the vector matrix multiplication and the numerical integration of the anharmonic potential. The anharmonic potential is multiplied point-wise with the corresponding weights, while  $\mathbf{V}_L$  is sequentially contracted with the normalized Hermite polynomials from the right side (this step has been implemented using matrix–matrix multiplications). The transformed vector is then contracted with Hermite polynomials from the left side where each of these operations yields the complete contribution from the anharmonic potential to  $\mathbf{V}_T$ . Next, the contributions from the  $\hat{U}$  and  $\hat{C}$  terms to  $\mathbf{V}_T$  are constructed by multiplication of  $\mathbf{V}_L$  with the corresponding one mode integrals, for  $\hat{U}$ , and the one and two mode integrals, for  $\hat{C}$ . These steps are repeated several times depending on the order of the expansion and the number of vibrational degrees of freedom. An additional complication arises with the  $\hat{C}$  term as the resulting combinations of integrals have to be multiplied with different elements of  $\mathbf{V}_L$  and contribute to several elements of  $\mathbf{V}_T$ . Once the matrix–vector multiplication is done, the algorithm continues. After the new Lanczos vector is constructed every other iteration, a complete reorthogonalization of the Lanczos vectors is carried out<sup>111,112</sup> in order to avoid spurious eigenvalues.<sup>113</sup>

## RESULTS AND DISCUSSION

The approach outlined here has been tested for two triatomic molecules, the normal isotopic species of  $\text{H}_2\text{O}$  and  $\text{CO}_2$ . For the



**Figure 2.** Structure of the full Hamiltonian matrix in the FBR for a  $XY_2$  ( $C_{2v}$  symmetry) molecule adding different contributions to  $\hat{\mathcal{H}}$ . (All the data was obtained using five basis functions per vibrational mode, and all the pictorial representations contain the contribution from the harmonic oscillator operator in their diagonal).

**Table 1.** Convergence of the Anharmonic Contribution to the Zero-Point Energy and the Low-Lying Vibrational Energy Levels of  $H_2^{16}O$  as Function of Number of Grid Points Used in the Numerical Integration (in  $cm^{-1}$ )<sup>a,b</sup>

states <sup>c</sup>	number of grid points per mode											
( $n_1$ $n_2$ $n_3$ )	7	11	17	20	25	27	29	31	33	35	37 <sup>d</sup>	ref 40
(0 0 0)	4657.55	<b>4649.22</b>	4649.22	4649.22	4629.22	4629.22	4629.22	4629.22	4629.22	4629.22	<b>4649.22</b>	4649.22
(0 1 0)	1593.01	<b>1582.46</b>	1582.46	1582.46	1582.46	1582.46	1582.46	1582.46	1582.46	1582.46	<b>1582.46</b>	1582.46
(0 2 0)	3127.22	3126.71	<b>3126.70</b>	3126.70	3126.70	3126.70	3126.70	3126.70	3126.70	3126.70	<b>3126.70</b>	3126.70
(1 0 0)	3657.86	<b>3656.95</b>	3656.95	3656.95	3656.95	3656.95	3656.95	3656.95	3656.95	3656.95	<b>3656.95</b>	3656.95
(0 0 1)	3742.66	<b>3742.57</b>	3742.57	3742.57	3742.57	3742.57	3742.57	3742.57	3742.57	3742.57	<b>3742.57</b>	3742.57
(0 3 0)	4636.84	4628.87	<b>4628.80</b>	4628.80	4628.80	4628.80	4628.80	4628.80	4628.80	4628.80	<b>4628.80</b>	4628.80
(1 1 0)	5224.42	5223.39	<b>5223.38</b>	5223.38	5223.38	5223.38	5223.38	5223.38	5223.38	5223.38	<b>5223.38</b>	5223.39
(0 1 1)	5281.41	<b>5281.31</b>	5281.31	5281.31	5281.31	5281.31	5281.31	5281.31	5281.31	5281.31	<b>5281.31</b>	5281.31
(0 4 0)	6147.68	6083.88	6082.54	6082.54	<b>6082.53</b>	6082.53	6082.53	6082.53	6082.53	6082.53	<b>6082.53</b>	6082.54
(1 2 0)	6756.61	6751.64	<b>6751.55</b>	6751.55	6751.55	6751.55	6751.55	6751.55	6751.55	6751.55	<b>6751.55</b>	6751.56
(0 2 1)	6784.44	<b>6783.89</b>	6783.89	6783.89	6783.89	6783.89	6783.89	6783.89	6783.89	6783.89	<b>6783.89</b>	6783.89
(2 0 0)	7218.12	7198.30	<b>7198.09</b>	7198.09	7198.09	7198.09	7198.09	7198.09	7198.09	7198.09	<b>7198.09</b>	7198.09
(1 0 1)	7241.67	7236.36	<b>7236.31</b>	7236.31	7236.31	7236.31	7236.31	7236.31	7236.31	7236.31	<b>7236.31</b>	7236.32
(0 0 2)	7425.65	7421.14	<b>7421.10</b>	7421.10	7421.10	7421.10	7421.10	7421.10	7421.10	7421.10	<b>7421.10</b>	7421.10
(0 5 0)	7774.51	7492.79	7477.54	7477.42	7477.37	7477.37	7477.37	7477.36	7477.37	7477.36	7477.37	7477.38 <sup>e</sup>
(1 3 0)	8253.40	8239.20	8237.88	8237.86	8237.85	8237.85	8237.85	8237.89	8237.85	8237.86	8237.85	8237.86
(0 3 1)	8273.14	8246.75	<b>8246.69</b>	8246.69	8246.69	8246.69	8246.69	8246.69	8246.69	8246.69	<b>8246.69</b>	8246.69
(2 1 0)	8756.47	8740.00	8739.74	<b>8739.73</b>	8739.73	8739.73	8739.73	8739.73	8739.73	8739.73	<b>8739.73</b>	8739.73
(1 1 1)	8764.15	8758.91	<b>8758.87</b>	8758.87	8758.87	8758.87	8758.87	8758.87	8758.87	8758.87	<b>8758.87</b>	8758.87
(0 6 0)	9893.84	8892.33	8796.29	8793.26	8792.19	8791.95	8791.34	8792.55	8791.65	8792.40	<b>8791.84</b>	8792.77 <sup>e</sup>
(0 1 2)	8930.91	8925.12	<b>8925.07</b>	8925.07	8925.07	8925.07	8925.07	8925.07	8925.07	8925.07	<b>8925.07</b>	8925.07

<sup>a</sup> Results obtained using the CVRQD potential energy surface of refs 40, 115, and 116. <sup>b</sup> Bold font was used when two digits convergence (in  $cm^{-1}$ ) was reached.

<sup>c</sup> The ordering of the vibrational modes is consistent with the standard spectroscopic criteria<sup>174</sup> i.e.,  $v_1$ : symmetric stretching;  $v_2$ : bending;  $v_3$ : asymmetric stretching. <sup>d</sup> Bold font was used in this column with states that converge with 37 or less number of grid points. Italic underlined refers to those states whose converged values were slightly different from ref 40 or were unconverged in the present study as well. <sup>e</sup> Eigenvalues with low convergence rates in the discrete variable representation approach of Mátyus et al.<sup>40</sup> Problems of convergence in this numerical method are underlined. Compare footnote of Table 1 in ref 40.

**Table 2.** Corrections to the Harmonic ZPE and Low-Lying Vibrational Transitions of H<sub>2</sub><sup>16</sup>O Resulting from Different Orders of the Expansion of the  $\hat{U}$  term (in cm<sup>−1</sup>)<sup>a</sup>

states <sup>b</sup>		order of the $\hat{U}$ term contribution <sup>c,d</sup>							
( <i>n</i> <sub>1</sub> <i>n</i> <sub>2</sub> <i>n</i> <sub>3</sub> )	harm	$\hat{U}^{(0)}$	$+\hat{U}^{(2)}$	$+\hat{U}^{(4)}$	$+\hat{U}^{(6)}$	$+\hat{U}^{(8)}$	$+\hat{U}^{(10)}$	$+\hat{U}^{(12)}$	$+\hat{U}^{(14)}$
(0 0 0)	4714.58	−12.88	−13.31	−13.33	<b>−13.34</b>	−13.34	−13.34	−13.34	−13.34
(0 1 0)	1649.20	—	−0.52	−0.59	<b>−0.60</b>	−0.60	−0.60	−0.60	−0.60
(0 2 0)	3298.40	—	−1.04	−1.23	−1.26	<b>−1.27</b>	−1.27	−1.27	−1.27
(1 0 0)	3834.44	—	−0.19	<b>−0.21</b>	−0.21	−0.21	−0.21	−0.21	−0.21
(0 0 1)	3945.53	—	−0.15	−0.16	<b>−0.17</b>	−0.17	−0.17	−0.17	−0.17
(0 3 0)	4947.59	—	−1.55	−1.92	−2.00	<b>−2.02</b>	−2.02	−2.02	−2.02
(1 1 0)	5483.63	—	−0.71	−0.82	−0.84	<b>−0.85</b>	−0.85	−0.85	−0.85
(0 1 1)	5594.73	—	−0.67	−0.76	−0.77	<b>−0.78</b>	−0.78	−0.78	−0.78
(0 4 0)	6596.79	—	−2.07	−2.66	−2.82	−2.86	<b>−2.88</b>	−2.88	−2.88
(1 2 0)	7132.83	—	−1.23	−1.49	−1.54	−1.54	<b>−1.56</b>	−1.56	−1.56
(0 2 1)	7243.93	—	−1.19	−1.41	−1.45	<b>−1.46</b>	−1.46	−1.46	−1.46
(2 0 0)	7668.87	—	−0.38	<b>−0.43</b>	−0.43	−0.43	−0.43	−0.43	−0.43
(1 0 1)	7779.97	—	−0.34	−0.38	<b>−0.39</b>	−0.39	−0.39	−0.39	−0.39
(0 0 2)	7891.07	—	−0.30	−0.33	−0.33	<b>−0.34</b>	−0.34	−0.34	−0.34
(0 5 0)	8245.99	—	−2.59	−3.45	−3.73	−3.82	−3.85	<b>−3.86</b>	−3.86
(1 3 0)	8782.03	—	−1.74	−2.20	−2.32	−2.36	<b>−2.37</b>	−2.37	−2.37
(0 3 1)	8893.13	—	−1.70	−2.11	−2.20	<b>−2.23</b>	−2.23	−2.23	−2.23
(2 1 0)	9318.07	—	−0.90	−1.06	<b>−1.10</b>	−1.10	−1.10	−1.10	−1.10
(1 1 1)	9429.17	—	−0.86	−1.00	−1.03	−1.03	<b>−1.04</b>	−1.04	−1.04
(0 6 0)	9895.19	—	−3.11	−4.30	−4.74	−4.90	−4.97	−5.00	<b>−5.00</b>
(0 1 2)	9540.26	—	−0.82	−0.94	<b>−0.96</b>	−0.96	−0.96	−0.96	−0.96

<sup>a</sup> Results obtained using 20 grid points and basis functions per degree of freedom. <sup>b</sup> The ordering of the vibrational modes is consistent with the standard spectroscopic criteria,<sup>174</sup> i.e.,  $\nu_1$ : symmetric stretching;  $\nu_2$ : bending;  $\nu_3$ : asymmetric stretching. <sup>c</sup> Odd orders have been omitted because their contributions are almost negligible. <sup>d</sup> Bold font was used when two digits convergence (in cm<sup>−1</sup>) was reached.

first, a high-accuracy potential energy surface is available, and its vibrational level structure has been extensively studied (a starting point in the literature can be found in ref 114), while the second, CO<sub>2</sub>, represents a prototype for linear systems. Additionally, the applicability for four-atom and low-symmetry molecules is illustrated by the prediction of the low-lying vibrational spectrum of the normal isotopic species of formyl fluoride (HFCO).

**Water.** The investigation of the low-lying vibrational structure of the most abundant isotopologue of water, H<sub>2</sub><sup>16</sup>O, was carried out with the semiglobal PES developed by Polyansky et al. (CVRQD).<sup>115,116</sup> The convergence of the ZPE and the 20 lowest vibrational transitions as a function of the number of quadrature points per degree of freedom used to describe the anharmonic contribution is shown in Table 1. As expected, fast convergence is observed for the ZPE and for the three fundamental vibrations. The ZPE and fundamentals converge using only 9–11 grid points per degree of freedom. Transitions involving higher excitation of the bending mode ( $\nu_2$ , 1<sub>02</sub>, 3<sub>0</sub>,  $n = 3, 4, 5, \dots$ ) were more difficult to converge due to the somewhat large amplitude character of this motion. With 19–20 grid points per degree of freedom all states are converged except for the third, fourth, and fifth overtones of  $\nu_2$ , i.e., (0,4,0), (0,5,0), and (0,6,0). The first, (0,4,0), required 27 basis functions per degree of freedom to converge, and the other two [(0,5,0) and (0,6,0)] could not be converged even with 37 basis functions per mode. The (0,6,0) state still shows a final uncertainty of 0.28 cm<sup>−1</sup> (see Table 1). Our results compare well with those obtained in a DVR by Mátyus et al.<sup>40</sup> The largest discrepancy is observed for the (0,6,0) transition with a difference between the DEWE approach,<sup>40,117</sup> and our results of the order of 1.5 cm<sup>−1</sup>

using the same number of basis functions as Mátyus et al.,<sup>40</sup> i.e., 20 quadrature points per degree of freedom (see Table 1).

Table 2 shows the corrections to the harmonic ZPE and vibrational transitions resulting from the different expansion orders of  $\hat{U}$  (i.e.;  $\hat{U}^{(0)}, \hat{U}^{(2)}, \hat{U}^{(4)}, \dots$ ), see eqs 22 and 23. It can be observed that all corrections decrease the energies and, as expected, that the zeroth-order contribution ( $\hat{U}^{(0)}$ ) is a constant correction to all the vibrational levels with a quantitatively relevant effect on the ZPE and, of course, no impact for transition energies. The correction to the ZPE due to the  $\hat{U}$  term converges at sixth-order ( $\hat{U}^{(n)}$ ,  $n = 0-6$ ) and differs by only  $-0.46$  cm<sup>−1</sup> from the corresponding zeroth-order correction usually applied in VPT2.<sup>94,118–120</sup> The corrections to the fundamentals also converge at sixth-order and their magnitudes range between  $-0.60$  and  $-0.17$  cm<sup>−1</sup>. States involving two and higher quanta excitations of the bending motion exhibit the largest corrections, i.e., 2–5 cm<sup>−1</sup> and require higher orders in the expansions because of the slow convergence (which is caused, in part, by both the large amplitude character of these states and the incipient singularity in  $\mu$  at linear geometries).<sup>121–123</sup> This behavior is typical for vibrations with large amplitude character<sup>124,125</sup> and can be used to identify this type of motion. The kinetic energy contributions resulting from  $\hat{C}$  are presented in Table 3; these corrections are characterized by positive contributions to the energies and relatively fast convergence. The  $\hat{C}^{(i)}$  corrections to the ZPE are significantly smaller than those due to  $\hat{U}$ . However, their quantitative influence on the vibrational states in general gains importance with increasing level of excitation. As expected, the zeroth-order correction,  $\hat{C}^{(0)}$ , is the leading contribution.



**Table 3.** Corrections to the Harmonic ZPE and Low-Lying Vibrational Transitions of  $\text{H}_2^{16}\text{O}$  Resulting from Different Orders of the Expansion of the  $\hat{C}$  Term (in  $\text{cm}^{-1}$ )<sup>a</sup>

states <sup>b</sup> ( $n_1 n_2 n_3$ )	harm	order of the $\hat{C}$ term contribution <sup>c,d</sup>			
		$\hat{C}^{(0)}$	$+\hat{C}^{(0)}$	$+\hat{C}^{(4)}$	$+\hat{C}^{(6)}$
(0 0 0)	4714.58	1.91	1.91	<b>1.92</b>	1.92
(0 1 0)	1649.20	13.30	<b>13.40</b>	13.40	13.40
(0 2 0)	3298.40	26.45	<b>26.64</b>	26.64	26.64
(1 0 0)	3834.44	<b>0.00</b>	0.00	0.00	0.00
(0 0 1)	3945.53	13.26	<b>13.36</b>	13.36	13.36
(0 3 0)	4947.59	39.45	<b>39.73</b>	39.73	39.73
(1 1 0)	5483.63	13.31	13.63	<b>13.64</b>	13.64
(0 1 1)	5594.73	53.02	53.40	<b>53.41</b>	53.41
(0 4 0)	6596.79	52.30	52.66	<b>52.67</b>	52.67
(1 2 0)	7132.83	26.45	27.05	<b>27.07</b>	27.07
(0 2 1)	7243.93	92.32	92.96	<b>92.97</b>	92.97
(2 0 0)	7668.87	0.00	<b>0.06</b>	0.06	0.06
(1 0 1)	7779.97	13.26	13.59	<b>13.60</b>	13.60
(0 0 2)	7891.07	26.53	<b>26.73</b>	26.73	26.73
(0 5 0)	8245.99	65.01	<b>65.46</b>	65.46	65.46
(1 3 0)	8782.03	39.45	40.31	<b>40.33</b>	40.33
(0 3 1)	8893.13	131.16	132.04	<b>132.05</b>	132.05
(2 1 0)	9318.07	13.31	13.86	<b>13.87</b>	13.87
(1 1 1)	9429.17	53.02	54.23	<b>54.26</b>	54.26
(0 6 0)	9895.19	77.59	78.11	<b>78.12</b>	78.12
(0 1 2)	9540.26	92.77	93.45	<b>93.46</b>	93.46

<sup>a</sup> Results obtained using 20 grid points and basis functions per degree of freedom. <sup>b</sup> The ordering of the vibrational modes is consistent with the standard spectroscopic criteria,<sup>174</sup> i.e.,  $\nu_1$ : symmetric stretching;  $\nu_2$ : bending;  $\nu_3$ : asymmetric stretching. <sup>c</sup> Odd orders have been omitted because their contributions are almost negligible. <sup>d</sup> Bold font was used when two digits convergence (in  $\text{cm}^{-1}$ ) was reached.

Fundamentals and ZPE converge at fourth order ( $\hat{C}^{(4)}$ ) and all the 20 states at sixth order ( $\hat{C}^{(6)}$ ). When both contributions to the kinetic energy ( $\hat{K}(q, \hat{p})$ ), i.e., the pseudopotential,  $\hat{U}^{(i)}$ , and the Coriolis terms,  $\hat{C}^{(i)}$ ,  $i = 1, 2, 3, \dots$ , are simultaneously taken into account the quantitative results are dominated by the  $\hat{C}^{(i)}$  corrections, while the convergence is slower for the  $\hat{U}^{(i)}$  contributions (see Table 4). Once the convergence of the kinetic energy contribution is achieved by reaching an appropriate order in the expansions, which is expected always for small amplitude motions, it can be used in conjunction with the contribution from the anharmonic potential to estimate the final vibrational levels, see Table 5. Our results agree well with those from the numerical procedure of Mátyus et al.,<sup>40</sup> with the exception of the states (0,5,0) and (0,6,0), for which numerical results show a very slow convergence and are affected by singularities in the pseudopotential contribution.<sup>121–123</sup>

**CO<sub>2</sub>.** Since the resonance between the symmetric stretching mode ( $\nu_1$ ) of carbon dioxide and the first overtone of its degenerate bending motion ( $2\nu_2$ ) was identified by Fermi,<sup>126</sup> this molecule became a famous problem in molecular spectroscopy. The isotopologue  $^{12}\text{C}^{16}\text{O}_2$  and some others were extensively studied experimentally; as a result of that it was possible to experimentally infer quartic<sup>127</sup> and sextic<sup>128–132</sup> force fields for this species. Ab initio calculations of the quartic force field of  $^{12}\text{C}^{16}\text{O}_2$  have been carried out at different levels of theory.<sup>133–139</sup> Recently, Rodríguez-García et al.<sup>139</sup> calculated

the PES of  $^{12}\text{C}^{16}\text{O}_2$  from a set of energy points computed using coupled-cluster methods with partial and full inclusion of triple excitation effects together with correlation-consistent basis sets and an extrapolation technique to converge to the basis set limit. They presented the PES in terms of a fourth-order Taylor expansion and by means of numerical values on a Gauss–Hermite quadrature grid.

Concerning the prediction of the vibrational spectrum, most theoretical studies were based on vibrational perturbation theory in second order (VPT2),<sup>133–137</sup> and fundamental transitions were the main focus of interest. ZPE and 13 vibrational states in the range of 2000–4900  $\text{cm}^{-1}$  were calculated within DVR using different quartic and sextic force fields<sup>131,132,138</sup> and a Hamiltonian expressed in terms of orthogonal Jacobi and Radau coordinates.<sup>140</sup> DVR was also used with a Hamiltonian in rectilinear normal coordinates,<sup>40</sup> and in this occasion, the ZPE and a total of 13 states between 600 and 2800  $\text{cm}^{-1}$  were predicted using the experimental sextic force field of Chédin.<sup>131</sup> Rodríguez-García et al.<sup>140</sup> applied the VSCF and VCI approaches with their extrapolated PES computing the lowest eight states of  $^{12}\text{C}^{16}\text{O}_2$  and analyzed the classic resonance  $\nu_1 \approx 2\nu_2$ .

In the present work we use Chédin's experimental quartic force field expressed in rectilinear normal coordinates.<sup>131</sup> Quintic and sextic force fields were excluded for two reasons: First, inconsistencies were previously found in the sign of some force constants in internal coordinates,<sup>138</sup> which have been confirmed in this research when expressing the force field in rectilinear normal coordinates,<sup>141</sup> and second, it has been demonstrated that the influence of the quintic and sextic potential in the low-energy region of the vibrational spectrum of  $^{12}\text{C}^{16}\text{O}_2$  is essentially negligible.<sup>140</sup> Considering the truncation of the potential expansion at the fourth order, we restrict our analysis to the ZPE and the eight lowest energy levels (see Table 6). The present results are compared with experimental values, from which the PES was derived and to results obtained with the VCI approach and the extrapolated PES,<sup>139</sup> as well as with the values calculated within DVR using Chédin's sextic force field in internal coordinates.<sup>131</sup> The third column of Table 6 contains the contribution from the vibrational Coriolis term,  $\hat{C}_{\text{linear}} = \sum_i \hat{C}_{\text{linear}}^{(i)}$  ( $i = 1, 2, 3, \dots$ ). In contrast to  $\text{H}_2^{16}\text{O}$ , the Coriolis contribution converges quickly and is essentially converged at zeroth-order ( $\hat{C}_{\text{linear}}^{(0)}$ ).<sup>142</sup> It is also noteworthy that the first and higher excitations of the symmetric stretch,  $\nu_1 [(n 0^0; 0), n = 1, 2, \dots]$  do not have contributions from this part of the KEO due to the fact that the Coriolis constants involving this mode ( $\xi_{\nu_1, \nu_{(2,3)}^x}, \xi_{\nu_1, \nu_{(2,3)}^y}$ ) vanish. Our results are close to the experimental values (mean deviation of about 1.0  $\text{cm}^{-1}$ ); the largest difference of about 3.0  $\text{cm}^{-1}$  for the (1 1 1 0) state probably is due to an insufficient inclusion of anharmonic effects and the computation of only “pure” vibrational states. Comparing with other theoretical predictions, the DVR calculations of Mátyus et al.<sup>40</sup> have a mean deviation of 1.1  $\text{cm}^{-1}$  with respect to experiment which, together with our results, confirms the small influence of higher-order force fields on the low-lying vibrational levels; Rodríguez-García et al.<sup>139</sup> obtained values with a mean deviation of about 3.0  $\text{cm}^{-1}$  from experiment using VCI and an extrapolated PES; their larger discrepancies might be partially due to the neglect of the vibrational Coriolis term in the kinetic energy operator. These contributions amount to 0.75–2.24  $\text{cm}^{-1}$ .

**HF<sub>2</sub>CO.** Several theoretical studies on the unimolecular dissociation and rearrangement reactions of HF<sub>2</sub>CO have been carried out over the years,<sup>143–149</sup> although to the best of our knowledge only two analytic representations of its global PES were constructed.<sup>148,149</sup> The first<sup>148</sup> was obtained by fitting 3855 energy

**Table 4.** Corrections to the Harmonic ZPE and Low-Lying Vibrational Transitions of H<sub>2</sub><sup>16</sup>O Resulting from Different Orders of the Expansion of the  $\hat{U}$  and  $\hat{C}$  Terms (in cm<sup>−1</sup>)<sup>a</sup>

states <sup>b</sup> ( <i>n</i> <sub>1</sub> <i>n</i> <sub>2</sub> <i>n</i> <sub>3</sub> )	harm	order of the $\hat{O} = \hat{U} + \hat{C}$ contribution <sup>c,d</sup>							
		$\hat{O}^{(0)}$	$+\hat{O}^{(2)}$	$+\hat{O}^{(4)}$	$+\hat{O}^{(6)}$	$+\hat{O}^{(8)}$	$+\hat{O}^{(10)}$	$+\hat{O}^{(12)}$	$+\hat{O}^{(14)}$
(0 0 0)	4714.58	−10.97	−11.38	<b>−11.41</b>	−11.41	−11.41	−11.41	−11.41	−11.41
(0 1 0)	1649.20	13.30	12.89	12.82	<b>12.81</b>	12.81	12.81	12.81	12.81
(0 2 0)	3298.40	26.45	25.61	25.43	<b>25.39</b>	25.39	25.39	25.39	25.39
(1 0 0)	3834.44	0.00	−0.16	<b>−0.18</b>	−0.18	−0.18	−0.18	−0.18	−0.18
(0 0 1)	3945.53	13.26	13.21	<b>13.20</b>	13.20	13.20	13.20	13.20	13.20
(0 3 0)	4947.59	39.45	38.19	37.83	37.75	<b>37.73</b>	37.73	37.73	37.73
(1 1 0)	5483.63	13.31	12.92	12.82	12.80	<b>12.79</b>	12.79	12.79	12.79
(0 1 1)	5594.73	53.02	52.75	52.66	<b>52.65</b>	52.65	52.65	52.65	52.65
(0 4 0)	6596.79	52.30	50.61	50.03	49.87	49.83	49.82	<b>49.81</b>	49.81
(1 2 0)	7132.83	26.45	25.84	25.59	25.53	25.52	25.52	<b>25.51</b>	25.51
(0 2 1)	7243.93	92.32	91.79	91.59	91.55	<b>91.54</b>	91.54	91.54	91.54
(2 0 0)	7668.87	0.00	−0.32	<b>−0.37</b>	−0.37	−0.37	−0.37	−0.37	−0.37
(1 0 1)	7779.97	13.26	13.25	13.22	<b>13.21</b>	13.21	13.21	14.21	14.21
(0 0 2)	7891.07	26.53	26.43	<b>26.41</b>	26.41	26.41	26.41	26.41	26.41
(0 5 0)	8245.99	65.01	62.89	62.04	61.77	61.68	61.65	<b>61.64</b>	61.64
(1 3 0)	8782.03	39.45	38.58	38.14	38.02	37.99	37.98	<b>37.97</b>	37.97
(0 3 1)	8893.13	131.16	130.37	129.99	129.90	129.88	129.88	<b>129.87</b>	129.87
(2 1 0)	9318.07	13.31	12.96	12.81	12.78	12.78	<b>12.77</b>	12.77	12.77
(1 1 1)	9429.17	53.02	53.39	53.27	53.25	<b>53.24</b>	53.24	54.24	54.24
(0 6 0)	9895.19	77.59	75.03	73.86	73.43	73.26	73.20	<b>73.18</b>	73.18
(0 1 2)	9540.26	92.77	92.65	92.55	<b>92.53</b>	92.53	92.53	92.53	92.53

<sup>a</sup> Results obtained using 20 grid points and basis functions per degree of freedom. <sup>b</sup> The ordering of the vibrational modes is consistent with the standard spectroscopic criteria,<sup>174</sup> i.e.,  $\nu_1$ : symmetric stretching;  $\nu_2$ : bending;  $\nu_3$ : asymmetric stretching. <sup>c</sup> Odd orders have been omitted because their contributions are almost negligible. <sup>d</sup> Bold font was used when two digits convergence (in cm<sup>−1</sup>) was reached.

**Table 5.** Corrections to the ZPE and Low-Lying Vibrational Transitions of H<sub>2</sub><sup>16</sup>O Resulting from the  $\hat{U}$  and  $\hat{C}$  Contributions (in cm<sup>−1</sup>)<sup>a,b</sup>

states <sup>c</sup> ( <i>n</i> <sub>1</sub> <i>n</i> <sub>2</sub> <i>n</i> <sub>3</sub> )	$\hat{\mathcal{H}}_0 + \hat{V}_{\text{anh}}$		$\hat{\mathcal{H}}_0 + \hat{V}_{\text{anh}} + \hat{U}^{\text{conv}}$		$\hat{\mathcal{H}}_0 + \hat{V}_{\text{anh}} + \hat{U}^{\text{conv}}$		$\hat{\mathcal{H}}_0 + \hat{V}_{\text{anh}} + (\hat{U} + \hat{C})^{\text{conv}}$	
	this work	ref 40	this work	ref 40	this work	ref 40	this work	ref 40
(0 0 0)	4649.22	4629.22	4636.30	4636.30	4651.23	4651.23	4638.21	4638.21
(0 1 0)	1582.46	1582.46	1581.58	1581.58	1595.94	1595.94	1595.08	1595.08
(0 2 0)	3126.70	3126.70	3124.64	3124.64	3154.22	3154.22	3152.20	3152.20
(1 0 0)	3656.95	3656.95	3657.23	3657.23	3656.77	3656.77	3657.05	3657.05
(0 0 1)	3742.57	3742.57	3742.97	3742.98	3755.32	3755.32	3755.73	3755.73
(0 3 0)	4628.80	4628.80	4625.02	4625.02	4671.26	4671.26	4667.58 <sup>f</sup>	4667.57
(1 1 0)	5223.38	5223.39	5222.82	5222.82	5236.05	5236.05	5235.49	5235.49
(0 1 1)	5281.31	5281.31	5280.90	5280.90	5331.88	5331.88	5331.51	5331.51
(0 4 0)	<u>6082.53</u>	6082.54	6075.99	6075.94 <sup>e</sup>	6141.44	6141.44	6135.16 <sup>f</sup>	6135.10 <sup>e</sup>
(1 2 0)	6751.55	6751.56	6749.85	6749.85	6777.62	6777.63	6775.96 <sup>f</sup>	6775.97
(0 2 1)	6783.89	6783.89	6782.41	6782.41	6873.53	6873.53	6872.15	6872.15
(2 0 0)	7198.09	7198.09	7198.67	7198.68	7200.62	7200.62	7201.19	7201.19
(1 0 1)	7236.31	7236.32	7236.99	7236.99	7248.54	7248.55	7249.22	7249.22
(0 0 2)	7421.10	7421.10	7421.86	7421.86	7444.12	7444.12	7444.88	7444.88
(0 5 0)	7477.37	<u>7477.38<sup>d</sup></u>	7465.45	<u>7465.40<sup>e</sup></u>	7555.49	<u>7555.48<sup>d</sup></u>	<u>7544.40<sup>f</sup></u>	<u>7444.19<sup>e</sup></u>
(1 3 0)	<u>8237.85</u>	8237.86	8234.43	<u>8234.43<sup>e</sup></u>	8278.39	8278.39	8275.10 <sup>f</sup>	8275.10 <sup>e</sup>
(0 3 1)	8246.69	8246.69	8243.69	8243.69	8377.55	8377.55	8374.77	8374.77
(2 1 0)	8739.73	8739.73	8739.41	8739.45	8762.14	8762.14	8761.92	8761.92
(1 1 1)	8758.87	8758.87	8758.77	8758.77	8807.10	8807.10	8807.03	8807.03
(0 6 0)	<u>8793.26</u>	<u>8792.77<sup>d</sup></u>	8767.57	<u>8771.13<sup>e</sup></u>	8896.33	<u>8896.06<sup>d</sup></u>	<u>8873.56<sup>f</sup></u>	<u>8875.62<sup>e</sup></u>
(0 1 2)	8925.07	8925.07	8925.06	8925.06	9000.34	9000.34	9000.39	9000.40

<sup>a</sup> Results obtained using 20 grid points and basis functions per degree of freedom and with the expansion of the  $\hat{U}$  and  $\hat{C}$  terms up to the twelfth-order, i.e., conv = 12. <sup>b</sup> Digits underlined present problems of convergence when using 20 sampling points per degree of freedom in the anharmonic potential. <sup>c</sup> The ordering of the vibrational modes is consistent with the standard spectroscopic criteria,<sup>174</sup> i.e.,  $\nu_1$ : symmetric stretching;  $\nu_2$ : bending;  $\nu_3$ : asymmetric stretching. <sup>d</sup> Eigenvalues with low convergence rate in ref 40. <sup>e</sup> Digits underlined and extracted from ref 40 (third, fifth, seventh, and ninth columns) did not converge due to the singularity present in the operator  $\hat{U}$ . <sup>f</sup> Using 37 grid points/basis functions per degree of freedom these transitions are predicted at 4667.58, 6135.16, 6775.96, 7544.37, 8275.10, and 8870.99 cm<sup>−1</sup> for (0,3,0), (0,4,0), (1,2,0), (0,5,0), and (0,6,0), respectively.

points calculated at the MP4<sup>150</sup> level of theory, and the second<sup>149</sup> was based on approximately 4000 energy points calculated at the MP2 level<sup>151</sup> using a (10s5p2d/5s2p)/[4s3p2d/3s2p] and a

correlation consistent polarized valence triple- $\zeta$  (cc-pVTZ) basis sets.<sup>152</sup> The MP2 PES was constructed by splitting and treating the energy surface in three different parts, each one describing a

**Table 6.** Final Results for the Prediction of the ZPE and Low-Lying Vibrational Transitions of  $^{12}\text{C}^{16}\text{O}_2$  (in  $\text{cm}^{-1}$ )<sup>a</sup>

states <sup>b</sup> ( $n_1 n_2^{  } n_3$ )	this work <sup>c,d</sup>			exp.		calcd <sup>e</sup>	
	$\hat{\mathcal{H}}_0$	$\hat{\mathcal{H}}_0 + \hat{V}_{\text{anh}}$	total	ref 131	ref 40	ref 139	
(0 0 <sup>0</sup> 0)	2548.05	2535.80	2536.15		2535.45		
(0 1 <sup>1</sup> 0)	672.89	666.73	667.47 (−0.09)	667.38	667.68 (−0.30)	669.1 (−1.72)	
(0 1 <sup>1</sup> 0)	672.89	666.73	667.47 (−0.09)	667.38	667.68 (−0.30)	669.1 (−1.72)	
(1 0 <sup>0</sup> 0)	1353.78	1284.30	1285.10 (−0.93)	1284.17	1284.98 (−0.81)	1288.9 (−4.73)	
(0 2 <sup>2</sup> 0)	1345.79	1334.48	1335.95 (−0.82)	1335.13	1336.48 (−1.35)	1339.6 (−4.47)	
(0 2 <sup>2</sup> 0)	1345.79	1334.48	1335.95 (−0.82)	1335.13	1336.48 (−1.35)	1339.6 (−4.47)	
(0 2 <sup>0</sup> 0)	1345.79	1387.29	1387.93 (0.26)	1388.19	1387.46 (0.73)	1389.3 (−1.11)	
(1 1 <sup>1</sup> 0)	2026.67	1928.03	1929.56 (2.91)	1932.47	1932.37 (0.10)	1938.0 (−5.53)	
(1 1 <sup>1</sup> 0)	2026.67	1928.03	1929.56 (2.91)	1932.47	1932.37 (0.10)	1938.0 (−5.53)	
(0 3 <sup>3</sup> 0)	2018.68	2003.07	2005.25 (−1.97)	2003.28	2006.43 (−3.15)	2011.4 (−8.12)	
(0 3 <sup>3</sup> 0)	2018.68	2003.07	2005.25 (−1.97)	2003.28	2006.43 (−3.15)	2011.4 (−8.12)	
(0 3 <sup>1</sup> 0)	2018.68	2076.81	2078.15 (−1.29)	2076.86	2076.27 (0.59)	2080.0 (−3.14)	
(0 3 <sup>1</sup> 0)	2018.68	2076.81	2078.15 (−1.29)	2076.86	2076.27 (0.59)	2080.0 (−3.14)	
(0 0 <sup>0</sup> 1)	2396.53	2347.87	2349.38 (−0.18)	2349.20	2347.32 (1.88)	2349.2 (0.00)	

<sup>a</sup> Results obtained with 14 grid points and basis functions per degree of freedom. <sup>b</sup> The ordering of the normal modes is: symmetric stretching,  $\nu_1$ ; degenerate bending motion,  $\nu_2$ ; asymmetric stretching,  $\nu_3$ . <sup>c</sup> Numbers in parentheses and italic are the differences from the experimental values.

<sup>d</sup> According to eqs 10, 11, and 15, the total pure vibrational Hamiltonian can be written as a sum of three terms, i.e.,  $\hat{\mathcal{H}} = \hat{\mathcal{H}}_0 + \hat{C}_{\text{linear}} + \hat{V}_{\text{anh}}$ . “Total” denotes the complete Hamiltonian including all three contributions. The  $\hat{C}_{\text{linear}}$  term was converged in zeroth-order.

**Table 7.** Corrections to the ZPE and Low-Lying Vibrational Transitions of HFCO Resulting from the  $\hat{U}$  and  $\hat{C}$  Contributions (in  $\text{cm}^{-1}$ )<sup>a,b</sup>

states <sup>c</sup> ( $n_1 n_2 n_3 n_4 n_5 n_6$ )	$\hat{\mathcal{H}}_0 + \hat{V}_{\text{anh}}$				states <sup>c</sup> ( $n_1 n_2 n_3 n_4 n_5 n_6$ )	$\hat{\mathcal{H}}_0 + \hat{V}_{\text{anh}}$			
	$+\hat{U}^{\text{conv}}$	$+\hat{C}^{\text{conv}}$	$+(\hat{U} + \hat{C})^{\text{conv}}$			$+\hat{U}^{\text{conv}}$	$+\hat{C}^{\text{conv}}$	$+(\hat{U} + \hat{C})^{\text{conv}}$	
(0 0 0 0 0 0)	4541.5	4540.6	4542.6	4541.7					
(0 0 0 0 1 0)	657.7	657.7	658.1	658.1	(0 1 0 1 0 0)	2862.4	2862.4	2863.9	2863.9
(0 0 0 0 0 1)	1014.2	1014.2	1019.2	1019.2	(0 0 0 0 3 1)	2979.3	2979.3	2986.7	2986.7
(0 0 0 1 0 0)	1048.9	1048.9	1049.5	1049.5	(1 0 0 0 0 0)	2999.4	2999.4	3003.2	3003.2
(0 0 0 0 2 0)	1314.0	1313.9	1314.8	1314.8	(0 0 0 1 3 0)	2994.1	2994.1	2996.4	2996.4
(0 0 1 0 0 0)	1369.5	1369.5	1370.3	1370.3	(0 0 0 0 0 3)	3021.5	3021.5	3036.8	3036.8
(0 0 0 0 1 1)	1670.7	1670.7	1676.5	1676.5	(0 0 1 0 1 1)	3042.3	3042.3	3049.5	3049.5
(0 0 0 1 1 0)	1698.8	1698.8	1699.9	1699.9	(0 0 1 1 1 0)	3060.8	3060.8	3063.2	3063.2
(0 1 0 0 0 0)	1820.7	1820.8	1821.3	1821.3	(0 0 0 1 0 2)	3062.7	3062.7	3074.4	3074.4
(0 0 0 0 3 0)	1968.7	1968.7	1970.0	1970.0	(0 0 0 2 0 1)	3090.4	3090.4	3098.0	3098.0
(0 0 1 0 1 0)	2027.3	2027.3	2028.3	2028.3	(0 0 0 3 0 0)	3107.8	3107.9	3109.6	3109.6
(0 0 0 0 0 2)	2021.2	2021.2	2031.4	2031.5	(0 1 0 0 2 0)	3124.1	3124.1	3126.2	3126.2
(0 0 0 1 0 1)	2059.1	2059.1	2065.4	2065.4	(0 1 1 0 0 0)	3189.3	3189.3	3190.7	3190.7
(0 0 0 2 0 0)	2084.2	2084.2	2085.3	2085.3	(0 0 0 0 5 0)	3273.8	3273.8	3275.9	3275.9
(0 0 0 0 2 1)	2325.8	2325.7	2332.4	2332.4	(0 0 0 0 2 2)	3330.2	3330.2	3343.3	3343.3
(0 0 0 1 2 0)	2347.2	2347.2	2349.0	2348.9	(0 0 1 0 3 0)	3337.1	3337.1	3338.6	3338.6
(0 0 1 0 0 1)	2385.8	2385.8	2392.2	2392.2	(0 0 0 1 2 1)	3354.9	3354.9	3363.2	3363.2
(0 0 1 1 0 0)	2411.5	2411.5	2412.9	2412.9	(0 0 0 2 2 0)	3367.1	3367.1	3369.7	3369.7
(0 1 0 0 1 0)	2473.1	2473.1	2474.4	2474.4	(0 0 2 0 1 0)	3373.0	3373.0	3375.3	3375.3
(0 0 0 0 4 0)	2621.7	2621.8	2623.5	2623.5	(0 0 1 0 0 2)	3394.6	3394.6	3406.4	3406.4
(0 0 1 0 2 0)	2683.1	2683.1	2684.4	2684.4	(0 0 1 1 0 1)	3423.6	3423.6	3431.4	3431.4
(0 0 0 0 1 2)	2676.4	2676.4	2688.1	2688.1	(0 0 1 2 0 0)	3440.0	3440.1	3441.9	3442.0
(0 0 0 1 1 1)	2707.7	2707.7	2715.0	2715.0	(0 1 0 0 1 1)	3478.4	3478.4	3485.6	3485.6
(0 0 2 0 0 0)	2715.0	2715.0	2716.7	2716.7	(0 1 0 1 1 0)	3507.2	3507.2	3509.6	3509.6
(0 0 0 2 1 0)	2726.4	2726.3	2728.2	2728.2	(0 2 0 0 0 0)	3622.4	3622.4	3623.7	3623.7
(0 1 0 0 0 1)	2827.1	2827.1	2833.3	2833.3	(0 0 0 0 4 1)	3631.1	3631.1	3639.3	3639.3

<sup>a</sup> Results obtained using 10 grid points and basis functions per degree of freedom and with expansion of the  $\hat{U}$  and  $\hat{C}$  terms up to second order, i.e., conv = 2. Digits underlined present problems of convergence. <sup>b</sup> Potential energy surface from ref 149. <sup>c</sup> The ordering of the vibrational normal modes follow the standard spectroscopic criteria,<sup>174</sup> i.e., the first five vibrations are those with  $a'$  symmetry and the last one is the out-of-plane bending motion ( $a''$  symmetry). The vibrational characterization is:  $\nu_1$ (CH-str);  $\nu_2$ (CO-str);  $\nu_3$ (CH bend);  $\nu_4$ (CF-str);  $\nu_5$ (FCO bend).

particular region of the PES, i.e., equilibrium, transition state, and asymptotic regions. In the present study, we use Yamamoto and Kato's PES<sup>149</sup> which enables comparison of our results with those obtained by other methods<sup>153–160</sup> that employed the same potential.

Theoretical predictions of the bound region of the vibrational spectrum of HFCO have been carried out using both perturba-

tional<sup>161,162</sup> and variational or pseudovariational<sup>153,154,158–160</sup> methods. However, the studies applying vibrational perturbation theory in second order (VPT2)<sup>163</sup> calculated only fundamentals<sup>161,162</sup> and a few two-quanta transitions ( $2\nu_2$ ,  $2\nu_4$ , and  $\nu_4 + \nu_5$ ).<sup>161</sup> Leforestier et al.<sup>153,154</sup> were probably among the first who applied other types of approaches for computing vibrational states of HFCO up to 5000  $\text{cm}^{-1}$ . Their initial study<sup>153</sup> was

based on a six-dimensional Hamiltonian expressed in Jacobi coordinates using a DVR of the Hamiltonian matrix contracted by a pseudospectral method.<sup>164</sup> In a second paper, they proposed the Jacobi–Wilson (JW) method<sup>154</sup> using HFCO as a test molecule. Later, the same authors employed the JW approach in combination with a modified Davidson algorithm based on a prediagonalization–perturbation step and calculated the lowest 350 vibrational states of  $a'$  symmetry<sup>158</sup> and the high-energy overtones of the out-of-plane mode ( $\nu_6$ ) (6400–10900  $\text{cm}^{-1}$ ).<sup>157</sup> The latter spectral region was also investigated by means of the multiconfiguration time-dependent Hartree (MCTDH) method.<sup>159</sup> By contrast, the approach presented here is expected to provide a suitable description of the low energy range, and its compact form facilitates its use with medium and large molecules as well as different bonding arrangements.

Results obtained in the present research for the ZPE and the 50 lowest vibrational transitions of formyl fluoride are presented in Table 7. For this molecule, expansions of the pseudopotential and Coriolis terms converge very rapidly; both contributions are already converged at the second order of the Taylor expansion.<sup>142</sup> It can also be observed that the effect of the  $\hat{U}$  term is essentially negligible, except for the zero-point energy which is lowered by 0.9  $\text{cm}^{-1}$  by this correction. This indicates that HFCO is a quite rigid molecule. By contrast, the Coriolis term has a larger quantitative influence; for most of the states its contribution ranges from 1 to 10  $\text{cm}^{-1}$  and for some higher quanta transitions involving the out-of-plane mode,  $\nu_6$ , the Coriolis term contributes 10–15  $\text{cm}^{-1}$ ; see in Table 7 cases as, for example,  $2\nu_6$ ,  $\nu_5 + 2\nu_6$ ,  $3\nu_6$ ,  $\nu_4 + 2\nu_6$ ,  $2\nu_5 + 2\nu_6$ , and  $\nu_3 + 2\nu_6$ .

The transition energies calculated in this work were compared with results obtained using other theoretical approaches, see Table 8. Nevertheless the earliest studies<sup>153,154</sup> have been omitted because some problems have subsequently been found in those calculations.<sup>158,160</sup> Thus, Table 8 contains the ZPE and transition energies calculated by the JW method coupled to a modified Davidson scheme,<sup>158</sup> those obtained with the MCTDH approach,<sup>159</sup> and finally the values recently computed by Wang et al.<sup>160</sup> in their rovibrational study of HFCO based on a direct product of rotational Wigner functions and a DVR of the vibrational part. In references 158 and 160 the KEO was expressed in terms of Jacobi vectors, while valence polyspherical coordinates were used with the MCTDH method.<sup>159</sup> Our results agree well with those obtained for the  $a'$ -transitions calculated by the JW approach<sup>158</sup> and with the fundamental frequencies estimated with the MCTDH method;<sup>159</sup> the largest discrepancies are 1.0 and 1.7  $\text{cm}^{-1}$  for the CH stretching and the ZPE, respectively. The fundamental vibrations predicted by DVR and FBR in the rovibrational study of Wang et al.<sup>160</sup> are slightly higher than the results of this work; these differences might be related with the constraints on the bond angles made in ref 160 in order to eliminate artifacts of the Yamamoto et al.'s surface.<sup>149</sup> Concerning the experimental values, although several experiments were devoted to the highly excited vibrational levels of HFCO (above 14 000  $\text{cm}^{-1}$ ),<sup>165–167</sup> no intensive research has been carried out on the low-energy region of the vibrational spectrum of this molecule. The earliest and almost only infrared and Raman experimental studies assigned the five  $a'$  fundamentals and a few higher quanta transitions ( $2\nu_2$ ,  $2\nu_4$ ,  $3\nu_4$ ,  $4\nu_4$ ,  $\nu_3 + \nu_4$ ,  $\nu_3 + \nu_5$ , and  $\nu_4 + \nu_5$ ) but could only provide tentative assignments of the out-of-plane bending mode,  $\nu_6$ .<sup>168–170</sup> It was not until 1978,<sup>171</sup> and later confirmed by stimulated emission pumping spectroscopy,<sup>165–167</sup> that this  $a''$ -symmetry motion was assigned to a wavenumber of 1011.2  $\text{cm}^{-1}$ . Beside these experiments, some high-resolution laser Stark measurements of  $\nu_2$  (C=O stretch) were done,<sup>172</sup> and the

**Table 8.** Calculated ZPE and Experimental and Calculated Low-Lying Vibrational Transitions of HFCO in the Spectral Range Between 0 and 3660  $\text{cm}^{-1}$  (in  $\text{cm}^{-1}$ )<sup>a</sup>

no. <sup>c</sup>	states <sup>b</sup> ( $n_1 n_2 n_3 n_4 n_5 n_6$ )	calcd					exp. <sup>h</sup>
		JW <sup>d</sup>	MCTDH <sup>e</sup>	DVR <sup>f</sup>	FBR <sup>f</sup>	This work <sup>g</sup>	
0	(0 0 0 0 0)		4540.0	4542.58	4542.56	4541.7	
1	(0 0 0 0 1 0)	658.1	658.1	659.39	659.37	658.1	662.6
2	(0 0 0 0 0 1)		1019.1	1019.43	1019.43	1019.2	1011.2
3	(0 0 0 1 0 0)	1049.5	1049.5	1050.45	1050.42	1049.5	1064.9
4	(0 0 0 0 2 0)		1314.8			1314.8	1324.1
5	(0 0 1 0 0 0)	1370.2	1370.3	1370.34	1370.33	1370.3	1342.3
7	(0 0 0 1 1 0)	1699.9				1699.9	1719.3
8	(0 1 0 0 0 0)	1821.3	1821.4	1822.17	1822.14	1821.4	1836.8
13	(0 0 0 2 0 0)	2085.4				2085.3	2115.6
17	(0 0 1 1 0 0)	2412.8				2412.9	2412.0
18	(0 1 0 0 1 0)	2474.3				2474.4	2494.2
25	(0 1 0 0 0 1)					2833.3	2841.0
26	(0 1 0 1 0 0)	2863.8				2863.9	2895.0
28	(1 0 0 0 0 0)	3003.1	3003.2	3004.97	3005.08	3003.2	2981.2
37	(0 1 0 0 2 0)	3126.1				3126.2	3150.6
49	(0 2 0 0 0 0)	3623.5				3623.6	3652.8

<sup>a</sup> Results obtained using 10 grid points per degree of freedom and with expansion of the  $\hat{U}$  and  $\hat{C}$  terms up to second order, i.e.,  $\text{conv} = 2$ . <sup>b</sup> The ordering of the vibrational normal modes follows the standard spectroscopic criteria,<sup>174</sup> i.e., the first five vibrations are those with  $a'$  symmetry and the last one is the out-of-plane bending motion ( $a''$  symmetry). The vibrational characterization is:  $\nu_1$ (CH-str);  $\nu_2$ (CO-str);  $\nu_3$ (CH bend);  $\nu_4$ (CF-str);  $\nu_5$ (FCO bend). <sup>c</sup> Ordering of the transitions in increasing value of energy. <sup>d</sup> JW stands for Jacobi–Wilson method used in ref 158. <sup>e</sup> MCTDH stands for multiconfiguration time-dependent Hartree method used in ref 159. <sup>f</sup> Ref 160. <sup>g</sup> The potential energy surface from ref 149 was employed. <sup>h</sup> Experimental values extracted from refs 153 and 154.

only new experimental data for two and higher quanta transitions come from indirect sources.<sup>153,154</sup> Thus, comparing our results with the scarce experimental information in the spectral range of 0–3650  $\text{cm}^{-1}$  (see Table 8), it can be seen that the calculated CO and CF stretchings ( $\nu_2$  and  $\nu_4$ , respectively) are about 15  $\text{cm}^{-1}$  lower than the observed frequencies, and the CH bend ( $\nu_3$ ) and stretch ( $\nu_1$ ) are overestimated by 28 and 23  $\text{cm}^{-1}$ , respectively. The differences in comparison with experiment become even larger for most of the nine two-quanta transition energies included in Table 8. These large discrepancies to experiments are essentially due of deficiencies in the MP2 PES.<sup>173</sup> Nevertheless the consistent level of agreement of our results with a wide variety of theoretical approaches confirms the reliability of our implementation.

## SUMMARY

In this paper we have presented a full configuration interaction method for calculating low-lying vibrational energy levels of semirigid molecules based on Watson's pure vibrational Hamiltonian that is suitable for small amplitude motions. It is characterized by a finite basis representation in conjunction with a general quasi-analytic scheme for the evaluation of the kinetic energy terms,  $\hat{U}$  and  $\hat{C}$ , expressed as Taylor expansions with respect to the rectilinear normal coordinates around the equilibrium configuration. The generality of this vibrational Hamiltonian allows application to a large range of molecules, and the quasi-analytic treatment, although being restricted to small amplitude motions, avoids the explicit use of geometries close to linearity and problems associated with that region by the singularity of the Watson term. Our approach has been tested for a set of prototype molecules, i.e.,



H<sub>2</sub>O, CO<sub>2</sub>, and HFCO; the results confirm the applicability and accuracy of the presented method, for example, for determining accurate ZPEs, which are of importance to thermochemistry.<sup>94</sup> In addition, our code also offers a mechanism for analyzing the performance of perturbational approaches based on Taylor expansions of the potential and kinetic energy operators up to arbitrary order.

## ■ ASSOCIATED CONTENT

**S Supporting Information.** Figures SI–SIII present the structure of the Hamiltonian matrix, **H**, due to the contributions from different orders of the pseudopotential term ( $\hat{U}$ ), the Coriolis term ( $\hat{C}$ ), and both of them ( $\hat{U} + \hat{C}$ ), respectively. This material is available free of charge via the Internet at <http://pubs.acs.org/>.

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