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Variational vibrational calculations using high-order anharmonic force fields†

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A simple variational procedure, termed DOPI for discrete variable representation—Hamiltonian in orthogonal coordinates—direct product basis–iterative diagonalization, is described and applied to compute low-lying vibrational band origins (VBOs) of the triatomic systems H_2O, CO_2, and N_2O, employing published empirical and theoretical sextic force fields. While in these cases no difficulties arise when quartic potentials are used, the limited range of applicability of 6th-order potentials presents difficulties for the variational determination of VBOs, in particular for the higher-lying bending states. For H_2O, transformation of quadratic and quartic force fields from simple bond stretching to Simons–Parr–Finlan (SPF) coordinates results in computed VBOs deviating less from experiment. This, however, does not hold for the VBOs computed from the transformed sextic force fields where the two representations provide highly similar results. While use of empirical quartic and sextic force fields result in a much better reproduction of experimental VBOs than that of *ab initio* force fields, especially at higher (fifth- and sixth-) order the empirical force constants, obtained through different refinement procedures, do not correspond to the associated derivatives of the potential energy surface (PES). Rotational constants characterizing low-lying vibrational states have been evaluated as expectation values using inertia tensor formulas in the Eckart and principal axis frames. Only the Eckart axes should be used for these computations and they yield accurate vibrationally averaged rotational constants.

1. Introduction

Due to considerable methodological developments of the last two decades, building partially on seminal early papers of Handy and co-workers [1], accurate variational description of the nuclear motion of even highly excited small quantum systems has become a relatively straightforward task [2]. For triatomic systems solution of the rovibrational problem was made particularly tractable by the introduction of the discrete variable representation (DVR) [3–10] of the Hamiltonian. For somewhat larger systems this and similar procedures have been applied with considerable success. Nowadays solution strategies have started to appear to not only the four- [11–20] but also the five- [21–23] and six-particle [24] problems.

Nevertheless, one old difficulty of nuclear motion computations, that of the representation of the potential energy surface (PES), still plagues applications of even the most sophisticated theoretical and computational procedures. For example, while for a triatomic system electronic structure computations on the order of 1000, about 10 per degrees of internal freedom, is usually sufficient for a good overall representation of the global PES [25], in order to obtain a similar precision for a 4-atomic molecule would require 10^6 computations, a truly formidable computational task even on today's powerful computers. The simplest way of avoiding this problem is offered by the traditional approach to PESs, namely the expansion of the potential in a Taylor series about a reference, usually the equilibrium, geometry. While such force field expansions [26, 27] may not provide a good representation of the PES for systems undergoing large-amplitude motions, for many systems of practical interest an

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†This paper is dedicated to Professor Nicholas C. Handy on the occasions of his retirement from the Department of Chemistry of Cambridge University, Cambridge, UK, and the conference in his honour entitled 'Molecular quantum mechanics: a no nonsense path to progress'. Professor Handy has been instrumental in many of the original developments related to anharmonic force fields, including their determination through analytic derivative techniques of electronic structure theory, and the variational computation of rovibrational energy levels.

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anharmonic force field representation of the PES should provide at least the first important stepping stone to understand the complex internal dynamics of the system.

A further development, as compared to the 1960s and 1970s when (higher-order) force field expansions first became popular [28–33], is the widespread availability of analytic derivatives of the electronic energy in several electronic structure codes [34, 35]. For example, Kállay *et al.* [36, 37] recently reported the availability of analytic first and second derivatives at cetain multireference configuration interaction (MR-CI), multireference coupled cluster (MR-CC), and the full configuration interaction (FCI) levels. Therefore, apart from cost, computation of force fields up to the sextic terms should present, even at high levels of electronic structure theory, little technical difficulty. Quartic force fields, the usual limit when anharmonic force fields are employed within the boundaries of second-order vibrational perturbation theory (VPT2) [38–43], have been computed for relatively large systems, e.g., for the 17-atom amino acid L-proline [44].

Nevertheless, it must be admitted that over the years higher-order force fields fall somewhat out of favor. For example, to our best knowledge [26] complete sextic force fields in internal coordinates are available only for a handful of triatomic systems, N_2O [45–48], CO_2 [49–52], and H_2O [53]. This disfavour is due to several factors. First, it is exceedingly difficult to determine accurate higher-order force constants strictly from experimental information. Therefore, this approach has been abandoned by experimentalists once the precision of *ab initio* anharmonic force fields [26] has been widely recognized. Second, force fields computed from electronic structure codes are in Cartesian representation and it is a nontrivial, though computationally easily tractable, task to transform these force fields to more meaningful representations, especially to those given in terms of curvilinear internal coordinates. Third, polynomial expansions are subject to limited ranges of applicability due to the eventual breakdown of the expansion. Fourth, it was observed a long time ago that quartic force fields give excellent frequencies when used with VPT2 formulas, a precision of 1–2 cm^{-1} in the frequencies is not unusual [54], but use of variational procedures resulted in much larger deviations from experiment. This is a somewhat unfortunate situation since variational procedures make the use of somewhat complex procedures [40, 53, 55] treating resonances unnecessary. Nevertheless, based on the methodological advancements related to variational treatments of the vibrational motion of molecules [56], renewing studies on the utility of force fields for the prediction of rovibrational dynamics and spectra seemed timely to us. We note the recent variational studies of Zúniga and co-workers [57–60] especially in this respect.

In this paper we investigate the expected precision of vibrational frequencies and vibrationally averaged rotational constants when computed from force fields of differing order and of differing standard coordinate representations. We restrict our attention to the triatomic systems N_2O, CO_2, and H_2O, for which complete sextic force fields are available from the literature. After the Introduction we give details concerning an exceedingly simple strategy for the variational solution of the triatomic vibrational problem (section 2). In section 3 we report results on vibrational frequencies and their accuracy obtained by this solution strategy and high-order force fields available to us for N_2O [45–48], CO_2 [49–52], and H_2O [53]. In section 4 the expectation values of the rotational constants in the first few vibrational states are compared when the wavefunctions correspond to different representations of the related PESs. The paper is ended with conclusions.

2. Simple variational solution of the triatomic vibrational motion problem

Several strategies exist to set up a matrix representation of a multidimensional vibrational Hamiltonian (see [11–24] and [61–65]). One of the simplest possible strategies, first advocated probably in [11], is as follows: the Hamiltonian is expanded in orthogonal (O) coordinates [66,67], its matrix is represented by the discrete variable representation (DVR) [3–7] coupled with a direct product (P) basis, and advantage is taken of the sparsity and the special structure of the resulting Hamiltonian matrix whose required eigenvalues can be determined extremely efficiently by variants of the iterative (I) Lanczos technique [68]. The resulting procedure is termed DOPI for DVR – Hamiltonian in O coordinates – P basis – iterative (sparse Lanczos) diagonalization. The DOPI procedure, described below only briefly as its elements have been discussed before, has been programmed up and used exclusively during this study of triatomic systems.

The vibrational Hamiltonian of triatomic molecules using the orthogonal Jacobi [69] or Radau [70] coordinates $\{R_1,R_2,\Theta\}$ can be written in atomic units as [67]

$$\hat{H} = -\frac{1}{2\mu_1}\frac{\partial^2}{\partial R_1^2} - \frac{1}{2\mu_2}\frac{\partial^2}{\partial R_2^2} - \left(\frac{1}{2\mu_1 R_1^2} + \frac{1}{2\mu_2 R_2^2}\right)\left(\frac{\partial^2}{\partial \Theta^2} + \cot\Theta\frac{\partial}{\partial\Theta}\right) + \hat{V}(R_1,R_2,\Theta) \quad (1)$$

where $\hat{V}$ is the potential energy operator, μ_1 and μ_2 are well-defined [67] mass-dependent constants, R_1

and R_2 denote two stretching-type coordinates, Θ is a bending-type coordinate, and the volume element for integration is $\sin\Theta dR_1 dR_2 d\Theta$.

A three-dimensional direct product basis $\{\chi_{n_1}(R_1)\chi_{n_2}(R_2)\Phi_\ell(\cos\Theta)\}_{n_1,n_2,\ell=0}^{N_1-1,N_2-1,L-1}$ is employed for setting up the matrix representation of $\hat{H}$. The Legendre–DVR basis $\{\Phi_\ell(\cos\Theta)\}_{\ell=0}^{L-1}$ is a natural choice for the description of the bending motion because Legendre polynomials $P_\ell(\cos\Theta)$ are the analytical eigenfunctions, with eigenvalues $\ell(\ell+1)$, of the Θ-dependent part of the kinetic energy operator. The corresponding DVR representation can be set up via the so-called transformation method. This involves a $\mathbf{Q}$ coordinate matrix with matrix elements $Q_{\ell,\ell'} = \langle P_\ell(\cos\Theta)|\cos\Theta|P_{\ell'}(\cos\Theta)\rangle$, and the quadrature points $\{q_i\}_{i=1}^{L}$ are the eigenvalues of the $\mathbf{Q}$ matrix, while the $\mathbf{T}$ transformation matrix is defined by the eigenvectors of the $\mathbf{Q}$ matrix. $\mathbf{T}$ transforms from finite basis representation (FBR) to DVR:

$$\begin{aligned}(\mathbf{K}_\Theta)_{n,n'} &= \langle\Phi_n(\cos\Theta)| -\left(\frac{\partial^2}{\partial\Theta^2}+\cot\Theta\frac{\partial}{\partial\Theta}\right)|\Phi_{n'}(\cos\Theta)\rangle\\ &= \sum_{\ell=0}^{L-1} T_{\ell,n}\,\ell(\ell+1)\,T_{\ell,n'}. \qquad (2)\end{aligned}$$

Note that an analytic formula is also available to determine $(\mathbf{K}_\Theta)_{n,n'}$ [7]. For the stretching coordinates R_1 and R_2 one can choose from several one-dimensional DVR basis, $\{\chi_{n_j}(R_j)\}_{n_j=0}^{N_j-1}$ with $\{q_{i_j}\}_{i_j=1}^{N_j}$ quadrature points. One can obtain the matrix elements of the corresponding differential operators,

$$(\mathbf{K}_{R_j})_{n_j,n_j'} = \left\langle \chi_{n_j}(R_j)\left| -\frac{1}{2\mu_j}\frac{\partial^2}{\partial R_j^2}\right|\chi_{n_j'}(R_j)\right\rangle, \qquad (3)$$

using exact analytical formulas [7]. Finally, the DVR representation of the remaining part of the kinetic energy operator matrix, $(\mathbf{R}_j^{-2})_{n_j,n_j'} = \langle\chi_{n_j}(R_j)|1/(2\mu_j R_j^2)|\chi_{n_j'}(R_j)\rangle$, can be calculated using the quadrature approximation,

$$(\mathbf{R}_j^{-2})_{n_j,n_j'} = \frac{1}{2\mu_j q_{n_j}^2}\delta_{n_j,n_j'}. \qquad (4)$$

Expressions (2)–(4) have been used exclusively during programming of the kinetic energy operator in the DVR representation.

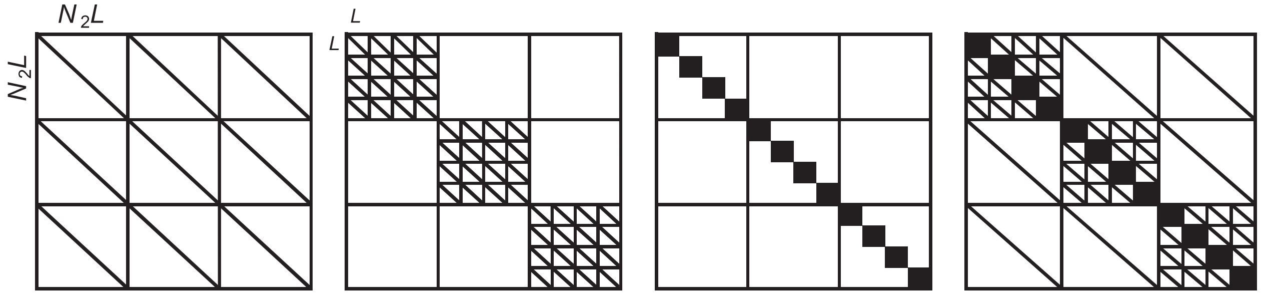
The form of the exact kinetic energy operator is the same for the different triatomic molecules, whether symmetric or nonsymmetric, linear or nonlinear, but this cannot be said about the approximate potential energy. Here advantage is taken of another simplifying aspect of the DVR representation, namely that the matrix of the potential energy operator $\hat{V}(R_1,R_2,\cos\Theta)$ is diagonal:

$$(\mathbf{V}^{\mathrm{diag}})_{n_1n_2\ell,n_1'n_2'\ell'} = V(q_{n_1},q_{n_2},q_\ell)\delta_{n_1n_2\ell,n_1'n_2'\ell'}. \qquad (5)$$

One can now build the $N_1N_2L\times N_1N_2L$-dimensional Hamiltonian matrix by computing direct products of matrices defined in equations (2)–(4) and adding the diagonal potential energy matrix to their sum:

$$\begin{aligned}\mathbf{H}^{\mathrm{DVR}} &= \mathbf{K}_{R_1}\otimes\mathbf{I}_{R_2}\otimes\mathbf{I}_\Theta + \mathbf{I}_{R_1}\otimes\mathbf{K}_{R_2}\otimes\mathbf{I}_\Theta\\ &\quad+\mathbf{R}_1^{-2}\otimes\mathbf{I}_{R_2}\otimes\mathbf{K}_\Theta + \mathbf{I}_{R_1}\otimes\mathbf{R}_2^{-2}\otimes\mathbf{K}_\Theta + \mathbf{V}^{\mathrm{diag}}.\end{aligned} \qquad (6)$$

In equation (6) $\mathbf{I}_{R_1}$, $\mathbf{I}_{R_2}$, and $\mathbf{I}_\Theta$ mean $N_1\times N_1$-, $N_2\times N_2$-, and $L\times L$-dimensional unit matrices, respectively. $\mathbf{H}^{\mathrm{DVR}}$ is a sparse matrix with $(N_1+N_2+L-2)N_1N_2L$ nonzero elements. (See figure 1 for a pictorial representation of the relevant matrices. Note that the third and fourth matrices on the right-hand side of equation (6) have the same structure.) In a typical application with $N_1 = N_2 = 50$ and $L = 100$ more than 99.9% of the matrix elements are zero. Consequently, one can easily diagonalize large (even orders beyond $100\,000\times100\,000$)



$\mathbf{K}_{R_1}\otimes\mathbf{I}_{R_2}\otimes\mathbf{I}_\Theta$ $\mathbf{I}_{R_1}\otimes\mathbf{K}_{R_2}\otimes\mathbf{I}_\Theta$ $\mathbf{R}_1^{-2}\otimes\mathbf{I}_{R_2}\otimes\mathbf{K}_\Theta$ $\mathbf{H}^{\mathrm{DVR}}$

Figure 1. Pictorial representation of the non-zero elements of the matrices appearing in Eq. (6) (for the sake of clarity, $N_1 = 3$ and $N_2 = 4$).

matrices using a Lanczos algorithm specialized for extremely sparse matrices.

Finally, note should be made of two more highly useful aspects of working in the DVR representation of the Hamiltonian. First, it is straightforward to delete undesirable basis functions as it simply means the neglect of the corresponding quadrature point. Second, in a DVR representation computation of expectation values of a function $f(R_1,R_2,\cos\Theta)$ is particularly simple,

$$\left\langle f(R_1,R_2,\cos\Theta)\right\rangle_v = \sum_{n_1,n_2,\ell=1}^{N_1,N_2,L} \left(C_{n_1 n_2 \ell,v}\right)^2 f(q_{n_1},q_{n_2},q_\ell), \quad (7)$$

where matrix $\mathbf{C}$ contains the eigenvectors of the $\mathbf{H}^{\mathrm{DVR}}$ matrix. The latter rewarding aspect of a DVR representation will be utilized in section 4.

The computer code DOPI3, written in FORTRAN and based upon the above simple procedure, can be obtained from the authors upon request [71].

3. Vibrational band origins from force field representations

The VBOs of H_2O, CO_2, and N_2O have been computed using published theoretical and empirical force field representations of the potential of these molecules given in the usual {STRE,STRE, BEND} representation, where STRE and BEND stand for the usual [72] simple bond stretching and angle bending coordinates, respectively, and the DOPI technique (see section 2). In the DOPI3 program we have used Hermite-DVR basis for the stretching coordinates and Legendre-DVR for the bend. The potential energy function has been built using force constants, of different representation and order, of the three triatomic molecules. For the only nonlinear molecule, H_2O, for convergence of the lowest 13 vibrational band origins (VBOs) to within 0.1 cm^{-1} the size of the DVR basis had to be increased only to 15 for the stretches and 25 for the bend, corresponding to a Hamiltonian matrix of dimension $5\,625 \times 5\,625$. It is important to note, however, that 25 basis functions for describing the bending motion of the linear molecules, CO_2 and N_2O, are not enough; in these cases the size of the Legendre–DVR basis had to be increased to 80 and a larger Hamiltonian matrix of dimension $18\,000 \times 18\,000$ had to be diagonalized. Due to the use of the efficient sparse Lanczos algorithm none of the diagonalizations took more than a few minutes on an average personal computer. None of the calculation used more than 30 Mb of memory.

Table 1. Zero-point energy (0 0 0) and the first 13 vibrational band origins of $H_2{}^{16}O$, in cm^{-1}, obtained from complete theoretical force fields of different order, with deviations from experiment, theory–experiment, given in parentheses.

	Quadratic		Quartic		Sextic[d]		
(v_1 v_2 v_3)	STRE[a]	SPF[b]	STRE[a]	SPF[b]	STRE[a]	SPF[b]	Expt.[c]
(0 0 0)	4694.0 (55.5)	4665.0 (26.5)	4646.2 (7.7)	4637.8 (−0.7)	4633.5 (−5.0)	4636.6 (−1.9)	4638.5
(0 1 0)	1659.3 (64.6)	1634.0 (39.3)	1600.6 (5.9)	1598.5 (3.8)	1594.4 (−0.3)	1594.4 (−0.3)	1594.7
(0 2 0)	3306.1 (154.5)	3255.3 (103.7)	3165.2 (13.6)	3160.6 (9.0)	3143.3 (−8.3)	3143.2 (−8.4)	3151.6
(1 0 0)	3842.9 (185.8)	3721.7 (64.6)	3709.9 (52.8)	3658.6 (1.5)	3654.6 (−2.5)	3654.3 (−2.8)	3657.1
(0 0 1)	3943.0 (187.1)	3813.2 (57.3)	3808.7 (52.8)	3755.2 (−0.7)	3752.5 (−3.4)	3751.9 (−4.0)	3755.9
(0 3 0)	4942.4 (275.6)	4864.9 (198.1)	4691.8 (25.0)	4684.3 (17.5)	4632.6 (−34.2)	4632.4 (−34.4)	4666.8
(1 1 0)	5529.0 (294.0)	5358.5 (123.5)	5299.0 (64.0)	5240.6 (5.6)	5229.1 (−5.9)	5228.3 (−6.7)	5235.0
(0 1 1)	5613.7 (282.4)	5433.6 (102.3)	5394.9 (63.6)	5334.7 (3.4)	5327.3 (−4.0)	5326.4 (−4.9)	5331.3
(0 4 0)	6569.2 (435.2)	6463.2 (329.2)	6177.1 (43.1)	6166.0 (32.0)	[6213.0]	[6241.7]	6134.0
(1 2 0)	7197.7 (422.6)	6980.0 (204.9)	6852.6 (77.5)	6785.8 (10.7)	6756.6 (−18.5)	6755.2 (−19.9)	6775.1
(0 2 1)	7271.0 (399.5)	7040.4 (168.9)	6947.4 (75.9)	6879.3 (7.8)	6860.2 (−11.3)	6858.9 (−12.6)	6871.5
(2 0 0)	7687.1 (485.6)	7375.7 (174.2)	7401.7 (202.2)	7210.2 (8.7)	7211.8 (10.3)	7195.0 (−6.5)	7201.5
(1 0 1)	7787.2 (537.4)	7427.9 (178.1)	7491.2 (241.3)	7258.1 (8.3)	7264.4 (14.6)	7242.6 (−7.2)	7249.8
(0 0 2)	7885.8 (440.8)	7579.8 (134.8)	7595.6 (150.6)	7446.0 (1.0)	7408.8 (−36.2)	7413.5 (−31.5)	7445.0

[a] STRE stands for a force field representation in {STRE,STRE,BEND} internal coordinates. It corresponds to the quartic Set II force field of table 3 of [53], computed at the aug-cc-pVQZ CCSD(T) level, augmented by Set I quintic and sextic constants of the same table, all computed at the non-stationary reference geometry of $r_{\mathrm{OH}} = 0.95843$ Å and $\alpha_{\mathrm{HOH}} = 104.44°$. The remaining forces are neglected in obtaining these results. The harmonic frequencies corresponding to this force field, obtained from a GF analysis, are $\omega_1 = 3828.9\,\mathrm{cm}^{-1}$, $\omega_2 = 1652.3\,\mathrm{cm}^{-1}$, and $\omega_3 = 3937.7\,\mathrm{cm}^{-1}$ [53]. Note that the sextic STRE VBOs were obtained after setting $f_{rrr'\alpha\alpha\alpha} = 0$ (see text).

[b] SPF stands for a force field representation in {SPF, SPF, BEND} internal coordinates using $r_e = 0.95843$ Å in the definition of the SPF coordinate (see the Appendix for the transformation formulas).

[c] The experimental vibrational band origins are taken from [83]. The ZPE value corresponds to the PES defined in [25].

[d] The higher vibrational states – in particular the bending-type terms – cannot be computed accurately due to the breakdown of the sextic potential as shown in figure 2.

Table 2. Zero-point energy (0 0 0) and the first 13 vibrational band origins of $^{12}C^{16}O_2$, in cm^{-1}, obtained from complete theoretical force fields of different order, with deviations from experiment, theory–experiment, given in parentheses.

	Quadratic		Quartic		Sextic		
$(v_1\ v_2\ v_3)$	STRE[a]	SPF[b]	STRE[a]	SPF[b]	STRE[a]	SPF[b]	Expt.[c]
(0 0 0)	2547.2	2533.9	2537.4	2526.3	2537.0	2526.3	
(1 0 0)	1267.2 (−18.2)	1260.9 (−24.5)	1276.9 (−8.5)	1274.1 (−11.3)	1276.9 (−8.5)	1274.6 (−10.8)	1285.4
(0 2 0)	1421.0 (32.8)	1410.0 (21.8)	1385.1 (−3.1)	1379.2 (−9.0)	1383.8 (−4.4)	1378.8 (−9.4)	1388.2
(0 0 1)	2408.8 (59.6)	2379.1 (29.9)	2370.6 (21.4)	2353.2 (4.0)	2368.1 (18.9)	2353.2 (4.0)	2349.2
(2 0 0)	2500.0 (−48.4)	2487.7 (−60.7)	2528.9 (−19.5)	2523.7 (−24.7)	2530.1 (−18.3)	2525.8 (−22.6)	2548.4
(1 2 0)	2702.8 (31.7)	2680.5 (9.4)	2671.1 (0.0)	2659.4 (−11.7)	2669.0 (−2.1)	2659.5 (−11.6)	2671.1
(0 4 0)	2870.1 (73.0)	2847.5 (50.4)	2784.4 (−12.7)	2773.6 (−23.5)	2780.8 (−16.3)	2771.9 (−25.2)	2797.1
(1 0 1)	3672.0 (59.2)	3631.2 (18.4)	3628.8 (16.0)	3607.3 (−5.5)	3624.7 (11.9)	3607.4 (−5.4)	3612.8
(0 2 1)	3828.0 (113.2)	3780.8 (66.0)	3738.6 (23.8)	3712.0 (−2.8)	3732.0 (17.2)	3711.5 (−3.3)	3714.8
(3 0 0)	3706.7 (−86.0)	3688.3 (−104.4)	3762.7 (−30.0)	3755.0 (−37.7)	3766.7 (−26.0)	3760.3 (−32.4)	3792.7
(2 2 0)	3959.8 (17.3)	3928.7 (−13.8)	3936.9 (−5.6)	3921.4 (−21.1)	3935.0 (−7.5)	3922.8 (−19.7)	3942.5
(1 4 0)	4144.3 (80.2)	4105.5 (41.4)	4063.8 (−0.3)	4043.9 (−20.2)	4058.8 (−5.3)	4043.4 (−20.7)	4064.1
(0 6 0)	4350.6 (125.6)	4314.5 (89.5)	4201.6 (−23.4)	4186.0 (−39.0)	4194.3 (−30.7)	4182.1 (−42.9)	4225.0
(0 0 2)	4817.5 (144.2)	4748.5 (75.2)	4722.0 (48.7)	4682.6 (9.3)	4713.2 (39.9)	4683.0 (9.7)	4673.3

[a] STRE stands for a force field representation in {STRE,STRE,BEND} internal coordinates. It corresponds to the quartic force field of table III of [49], computed at the QZ2P CCSD(T) level, employing the non-stationary reference geometry of $r_{CO} = 1.1600$ Å, augmented with TZ2P RHF quintic and sextic constants of the same table obtained at the same reference geometry. The remaining forces are neglected in obtaining the VBOs of this table. Note that the sextic STRE and SPF VBOs were obtained after changing the sign of $f_{\alpha\alpha\alpha\alpha\alpha\alpha}$.

[b] SPF stands for a force field representation in {SPF,SPF,BEND} internal coordinates using $r_e = 1.1600$ Å in the definition of the SPF coordinate (see the Appendix for the transformation formulas).

[c] The experimental vibrational band origins are taken from [84]. For the ZPE value see table 3.

Table 3. Zero-point energy (0 0 0) and the first 13 vibrational band origins of $^{12}C^{16}O_2$, in cm^{-1}, obtained from complete experimental force fields of different order, with deviations from experiment, calculation−experiment, given in parentheses.[a]

	Ref. [51]			Ref. [52]		Ref. [50]			
$(v_1\ v_2\ v_3)$	quadratic	quartic	sextic	quadratic	quartic	quadratic	quartic	sextic	Expt.
(0 0 0)	2543.5	2533.7	2532.9	2548.7	2537.1	2547.7	2536.0	2535.4	
(1 0 0)	1275.8(−9.6)	1286.8(1.4)	1285.1(−0.3)	1280.4(−5.0)	1286.5(1.1)	1279.2(−6.2)	1285.4(0.0)	1285.0(−0.4)	1285.4
(0 2 0)	1421.9(33.7)	1388.7(0.5)	1387.7(−0.5)	1426.3(38.1)	1390.0(1.8)	1425.2(37.0)	1389.0(0.8)	1387.5(−0.7)	1388.2
(0 0 1)	2392.0(42.8)	2349.2(0.0)	2346.4(−2.8)	2393.4(44.2)	2351.2(2.0)	2393.7(44.5)	2350.2(1.0)	2347.3(−1.9)	2349.2
(2 0 0)	2521.1(−27.3)	2553.1(4.7)	2547.5(−0.9)	2530.6(−17.8)	2549.9(1.5)	2528.1(−20.3)	2547.9(−0.5)	2547.6(−0.8)	2548.4
(1 2 0)	2701.8(30.7)	2677.9(6.8)	2671.8(0.7)	2709.7(38.6)	2674.5(3.4)	2707.9(36.8)	2672.3(1.2)	2669.4(−1.7)	2671.1
(0 4 0)	2877.9(80.8)	2800.7(3.6)	2798.8(1.7)	2887.2(90.1)	2802.2(5.1)	2884.9(87.8)	2799.8(2.7)	2795.3(−1.8)	2797.1
(1 0 1)	3664.5(51.7)	3615.9(3.1)	3610.7(−2.1)	3670.6(57.8)	3617.5(4.7)	3669.6(56.8)	3615.2(2.4)	3609.7(−3.1)	3612.8
(0 2 1)	3811.6(96.8)	3716.1(1.3)	3712.5(−2.3)	3817.4(102.6)	3721.0(6.2)	3816.6(101.8)	3718.5(3.7)	3710.7(−4.1)	3714.8
(3 0 0)	3740.6(−52.1)	3802.3(9.6)	3790.1(−2.6)	3755.2(−37.5)	3793.6(0.9)	3751.3(−41.4)	3791.1(−1.6)	3791.7(−1.0)	3792.7
(2 2 0)	3967.2(24.7)	3958.0(15.5)	3943.7(1.2)	3979.6(37.1)	3947.5(5.0)	3976.7(34.2)	3944.1(1.6)	3940.0(−2.5)	3942.5
(1 4 0)	4142.4(78.3)	4079.6(15.5)	4065.4(1.3)	4154.7(90.6)	4071.2(7.1)	4151.8(87.7)	4067.5(3.4)	4060.9(−3.2)	4064.1
(0 6 0)	4366.5(141.5)	4234.4(9.4)	4232.5(7.5)	4380.8(155.8)	4235.2(10.2)	4377.2(152.2)	4231.2(6.2)	4221.2(−3.8)	4225.0
(0 0 2)	4784.0(110.7)	4676.8(3.5)	4665.9(−7.4)	4786.8(113.5)	4681.0(7.7)	4787.3(114.0)	4678.5(5.2)	4667.9(−5.4)	4673.3

[a] The sextic VBOs were obtained after setting $\varepsilon_{\text{cut}} = 20\,000\,\text{cm}^{-1}$ (see text). All results reported correspond to {STRE,STRE,BEND} internal coordinates and $r_e(\text{CO}) = 1.1600$ Å. The experimental (Expt.) VBOs were obtained from [84].

The program system INTDER2000 [73–75] has been used for the exact, analytic transformation of internal coordinate force fields up to quartic terms from {STRE,STRE,BEND} to {SPF,SPF,BEND} representation, where SPF is the Simons–Parr–Finlan [76] coordinate. In the definition of the SPF [76] coordinate the respective r_e geometries have been used. Despite the availability of most relevant formulas [75], no general-purpose computer program exists for the exact transformation of derivatives beyond fourth order.

Table 4. Zero-point energy (0 0 0) and the first 13 vibrational band origins of $^{14}N_2{}^{16}O$, in cm^{-1}, obtained from complete theoretical force fields of different order, with deviations from experiment, theory–experiment, given in parentheses.

	Quadratic		Quartic		Sextic		
(v_1 v_2 v_3)	STRE[a]	SPF[b]	STRE[a]	SPF[b]	STRE[a]	SPF[b]	Expt.[c]
(0 0 0)	2441.1	2436.8	2425.4	2423.4	2425.0	2423.5	
(0 2 0)	1212.0(43.9)	1208.1(40.0)	1213.5(45.4)	1213.1(45.0)	1214.4(46.3)	1214.3(46.2)	1168.1
(1 0 0)	1353.1(68.2)	1346.0(61.1)	1307.8(22.9)	1305.8(20.9)	1306.2(21.3)	1305.7(20.8)	1284.9
(0 0 1)	2319.5(95.7)	2301.2(77.4)	2266.4(42.6)	2260.8(37.0)	2263.6(39.8)	2260.8(37.0)	2223.8
(0 4 0)	2392.8(70.2)	2384.6(62.0)	2406.6(84.0)	2405.4(82.8)	2410.6(88.0)	2410.4(87.8)	2322.6
(1 2 0)	2585.1(123.1)	2571.5(109.5)	2530.7(68.7)	2527.2(65.2)	2528.9(66.9)	2528.3(66.3)	2462.0
(2 0 0)	2722.4(159.1)	2706.1(142.8)	2614.2(50.9)	2608.5(45.2)	2609.4(46.1)	2608.5(45.2)	2563.3
(0 2 1)	3528.5(164.5)	3502.1(138.1)	3454.0(90.0)	3446.8(82.8)	3451.2(87.2)	3448.2(84.2)	3364.0
(0 6 0)	3551.9(85.3)	3538.8(72.2)	3550.7(84.1)	3538.6(72.0)	3542.1(75.5)	3538.7(72.1)	3466.6
(1 0 1)	3672.0(191.2)	3639.9(159.1)	3584.2(103.4)	3582.3(101.5)	3594.6(113.8)	3594.3(113.5)	3480.8
(1 4 0)	3786.8(165.9)	3766.9(146.0)	3729.5(108.6)	3724.3(103.4)	3730.3(109.4)	3729.6(108.7)	3620.9
(2 2 0)	3958.8(210.5)	3932.8(184.5)	3842.3(94.0)	3832.9(84.6)	3835.7(87.4)	3834.4(86.1)	3748.3
(3 0 0)	4113.3(276.9)	4085.7(249.3)	3922.1(85.7)	3910.9(74.5)	3912.6(76.2)	3911.1(74.7)	3836.4
(0 0 2)	4639.0(221.6)	4592.6(175.2)	4507.4(90.0)	4491.3(73.9)	4497.0(79.6)	4491.2(73.8)	4417.4

[a] STRE stands for a force field representation in {STRE,STRE,BEND} internal coordinates. It corresponds to the sextic force field of table 3 of [46], computed at the cc-pVTZ CCSD(T) level. The nonstationary reference structure is as follows: $r_{NN} = 1.1273$ Å and $r_{NO} = 1.1851$ Å. All force constants designated by *d* in table 3 of [46] were assumed to be zero. The remaining forces are neglected in obtaining these results.

[b] SPF stands for a force field representation in {SPF,SPF,BEND} internal coordinates using $r_e(NN) = 1.1273$ Å and $r_e(NO) = 1.1851$ Å in the definition of the appropriate SPF coordinates (see the Appendix for the transformation formulas).

[c] The experimental (Expt.) vibrational band origins are taken from [47]. For the ZPE value see table 5.

Table 5. Zero-point energy (0 0 0) and the first 13 vibrational band origins of $^{14}N_2{}^{16}O$, in cm^{-1}, obtained from complete experimental force fields of different order, with deviations from experiment, calculation–experiment, given in parentheses.

	Ref. [48]			Ref. [47]		Ref. [45]			
(v_1 v_2 v_3)	quadratic	quartic	sextic	quadratic	quartic	quadratic	quartic	sextic	Expt.
(0 0 0)	2386.3	2370.8	2370.8	2386.0	2370.2	2388.7	2370.1	2371.0	
(0 2 0)	1165.6(−2.5)	1168.5(0.4)	1168.7(0.6)	1165.5(−2.6)	1168.2(0.1)	1165.9(−2.2)	1166.6(−1.5)	1168.4(0.3)	1168.1
(1 0 0)	1329.2(44.3)	1287.0(2.1)	1285.8(0.9)	1329.3(44.4)	1286.3(1.4)	1329.1(44.2)	1283.9(−1.0)	1284.7(−0.2)	1284.9
(0 0 1)	2280.3(56.5)	2226.2(2.4)	2225.3(1.5)	2279.7(55.9)	2226.4(2.6)	2284.7(60.9)	2217.4(−6.4)	2223.3(−0.5)	2223.8
(0 4 0)	2300.6(−22.0)	2323.2(0.6)	2323.7(1.1)	2300.5(−22.1)	2322.5(−0.1)	2301.3(−21.3)	2319.1(−3.5)	2323.2(0.6)	2322.6
(1 2 0)	2520.6(58.6)	2465.9(3.9)	2464.4(2.4)	2520.6(58.6)	2464.4(2.4)	2520.7(58.7)	2460.0(−2.0)	2463.3(1.3)	2462.0
(2 0 0)	2668.4(105.1)	2569.9(6.6)	2565.9(2.6)	2668.6(105.3)	2567.6(4.3)	2668.2(104.9)	2563.1(−0.2)	2564.0(0.7)	2563.3
(0 2 1)	3414.1(50.1)	3367.6(3.6)	3368.3(4.3)	3413.8(49.8)	3367.0(3.0)	3415.1(51.1)	3349.4(−14.6)	3366.3(2.3)	3364.0
(0 6 0)	3443.1(−23.5)	3467.0(0.4)	3468.2(1.6)	3442.3(−24.3)	3465.8(−0.8)	3448.0(−18.6)	3461.0(−5.6)	3467.6(1.0)	3466.6
(1 0 1)	3609.1(128.3)	3490.8(10.0)	3485.7(4.9)	3608.5(127.7)	3489.6(8.8)	3613.5(132.7)	3465.4(−15.4)	3482.5(1.7)	3480.8
(1 4 0)	3676.3(55.4)	3627.0(6.1)	3624.7(3.8)	3676.3(55.4)	3625.2(4.3)	3676.7(55.8)	3617.7(−3.2)	3623.9(3.0)	3620.9
(2 2 0)	3875.8(127.5)	3758.9(10.6)	3753.3(5.0)	3876.0(127.7)	3755.2(6.9)	3875.8(127.5)	3747.7(−0.6)	3751.4(3.1)	3748.3
(3 0 0)	4023.2(186.8)	3850.5(14.1)	3841.8(5.4)	4023.4(187.0)	3845.4(9.0)	4022.7(186.3)	3838.9(2.5)	3839.3(2.9)	3836.4
(0 0 2)	4510.8(93.4)	4425.7(8.3)	4422.8(5.4)	4510.4(93.0)	4427.0(9.6)	4512.2(94.8)	4394.0(−23.4)	4418.4(1.0)	4417.4

[a] The VBOs computed from the sextic force field of Lacy and Whiffen [45] were obtained after setting $\varepsilon_{cut} = 15\,000\,cm^{-1}$ (see text). All results reported correspond to {STRE,STRE,BEND} internal coordinates. The reference structures are as follows: $r_e(NN) = 1.127292$ Å and $r_e(NO) = 1.185089$ Å [48], $r_e(NN) = 1.1282$ Å and $r_e(NO) = 1.1843$ Å [47], and $r_e(NN) = 1.12598$ Å and $r_e(NO) = 1.18624$ Å [45]. The experimental (Expt.) VBOs were obtained from [47].

Nevertheless, the explicit expressions for triatomic molecules, given in the Appendix, allowed this transformation to be carried out to sixth order.

The VBOs obtained for the parent isotopomers, the only ones considered in this study, of H_2O, CO_2, and N_2O are summarized in tables 1–5. Atomic masses [77] have been used throughout for the nuclear motion calculations.

For all three molecules studied the *ab initio* force fields have been obtained at non-stationary reference geo-

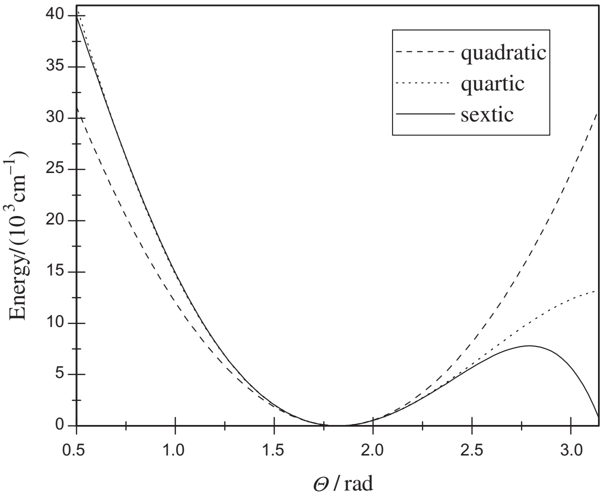


Figure 2. One-dimensional cuts of the potential energy surface representations of H_2O along the $\Theta = \alpha_{HOH}$ angle bending coordinate using {STRE,STRE,BEND} internal coordinates and bond stretching coordinates fixed at $r_e = 0.95843$ Å.

metries, corresponding to the best available estimates of the empirical equilibrium structures of the molecules at the time. In principle, compared to the traditional El'yashevich–Wilson GF or the VPT2 approaches, no difficulty arises from the existence of nonzero forces in the expansion of the potential when it is used in a variational solution of the nuclear motion problem. Therefore, one could avoid the non-zero force dilemma [74] hindering the general use of force fields obtained at nonstationary geometries. Since the *ab initio* force fields have been obtained at high levels of electronic structure theory, the remaining forces are usually rather small. Nevertheless, the effect of the inclusion of the forces in the potential on the VBOs is far from being negligible. For example, in the case of CO_2, where the remaining force is the largest, the change for the (0 0 0) and (2 0 0) VBOs, computed from the sextic STRE *ab initio* force field, is $+81\,\mathrm{cm}^{-1}$ and $-47\,\mathrm{cm}^{-1}$, respectively. The computed VBOs obtained neglecting all the forces are in all cases considerably closer to experiment than those obtained with the inclusion of the forces in the potential. Therefore, one important conclusion of this study is that remaining forces in the *ab initio* expansion of the potential should be neglected even in variational nuclear motion treatments. Consequently, results given in tables 1, 2, and 4 correspond to this choice, i.e. neglect forces in the expansion of the potential.

The next important question concerns the utility of including quintic and sextic constants in the expansion of the potential. The higher the order of the expansion the better the agreement is between the computed and the experimental VBOs. Especially gratifying is the improvement for $H_2{}^{16}O$, the lightest of the molecules considered and the only one with single bonds, which are well described by the CCSD(T) [78] (coupled cluster theory with single and double excitations augmented with a perturbational estimate of triple excitations) theory employed for the *ab initio* force field calculation. For the fundamental levels of H_2O obtained when the full sextic {STRE, STRE, BEND} force field is used to represent the potential the average error in reproducing the experimental fundamentals is $2.1\,\mathrm{cm}^{-1}$, while use of only the corresponding quartic expansion results in an average agreement not better than $37.2\,\mathrm{cm}^{-1}$. Therefore, it may seem worth expanding the potential beyond the quartic terms if a variational approach is employed for the calculation of the VBOs. Nevertheless, in almost all cases studied here use of the full sextic potential presented difficulties during the variational calculations of the VBOs due to the increased susceptibility of the potential to breakdown at quadrature points farther away from equilibrium. To illustrate this point a one-dimensional cut corresponding to the bending motion is presented for H_2O (figure 2). At 6th order it is not the stretching part of the potential that may cause considerable problems for the variational solution of the vibrational problem but the bending part. The sextic potential has a breakdown when the bending angle goes above 2.7 rad with a corresponding energy barrier as low as $7\,500\,\mathrm{cm}^{-1}$. This means that the higher VBOs, especially those involving more than three quanta in the bending, cannot be computed with high accuracy from the present force field representation of the potential. (The quartic force field expansion has no similar problem.) Nevertheless, convergence of the lower-lying VBOs can be achieved even if some of the Hamiltonian matrix elements have (somewhat) unreasonable values.

After a careful, term by term investigation of the sextic potentials it turned out that the apparent problems with obtaining converged eigenvalues can be eliminated by changing the values of certain force constants. In particular, in the case of H_2O setting $f_{rrr'\alpha\alpha\alpha} = 0$ solves the otherwise unsurmountable diagonalization problem. With this (nonphysical) choice all diagonalizations were successful giving converged results for the lower levels, though for the higher-lying bending states the VBOs could not be converged to better than a few cm^{-1}, while all other VBOs even with medium-size basis sets were converged to better than $0.01\,\mathrm{cm}^{-1}$. Therefore, in table 1 the sextic results presented for H_2O correspond to this choice and the problematic, only quasi-converged VBOs are given in brackets. For CO_2 the problematic force constant is $f_{\alpha\alpha\alpha\alpha\alpha\alpha}$, whose computed value is negative [49]. Setting this theoretical force constant to positive values solved the problem during determination of converged eigenvalues. However, this has not proved to be sufficient when experimental force fields have been used. Note also that $f_{\alpha\alpha\alpha\alpha\alpha\alpha}$ of CO_2 has been recomputed in this study at the all-electron aug-cc-pCVQZ [79] CCSD(T) level, where $f_{\alpha\alpha\alpha\alpha\alpha\alpha} = +193\,\mathrm{aJ\,rad^{-6}}$. For N_2O the empirical force field of Lacy and Whiffen [45], which contains several large unphysical coupling constants [46], seems to be extremely problematic in this respect. Here the diagonalization problem could not be solved by changing the sign of $f_{\alpha\alpha\alpha\alpha\alpha\alpha}$. Note also that for N_2O we were not able to reproduce the variational VBO results of Zúniga and co-workers [58], the deviations between the two sets of results are on the order of a few $\mathrm{cm^{-1}}$.

Another, perhaps more appealing solution to the problem of computing converged eigenvalues involves the introduction of a cutoff value, $\varepsilon_{\mathrm{cut}}$, employed in the following fashion: whenever the value of the potential calculated from the quadratic force field is larger than $\varepsilon_{\mathrm{cut}}$ at a quadrature point, the appropriate potential value is substituted by the corresponding harmonic value irrespective of the order of the force field actually employed. The practical problem with this approach is that it seems to protract the convergence of almost all of the VBOs and if it is chosen to be too low no convergence of the VBOs can be achieved. Nevertheless, it seems to lead to converged results in the cases investigated. Therefore, this solution was employed for the problematic computation of VBOs obtained from sextic empirical force fields of CO_2 and N_2O.

In line with a number of previous studies, when lower-order expansions of the potential are used, the agreement between experiment and theory becomes considerably better when the representation is changed from STRE to SPF coordinates. Again, especially pronounced is the improvement for the light H_2O molecule. However, when the full sextic force field is used to represent the potential of H_2O, the error in the prediction of the vibrational levels with up to 1 quantum in the bending mode is 9.1 and $7.3\,\mathrm{cm^{-1}}$ for the STRE and SPF representations, respectively. Therefore, another important result of this study is that the difference between the sextic STRE and SPF representations of the PES is hardly significant. This observation is in line with results obtained by Zúniga and co-workers for CO_2 and N_2O [57,58] and by us for N_2O. Furthermore, for the pure stretching VBOs the sextic SPF force field results in a slightly worse agreement with experiment than the quartic SPF field. Deviations between the quartic and sextic STRE and SPF force field results for CO_2 presented in table 2 can be traced to the treatment of residual forces during the computation of the VBOs. Namely, the SPF force fields employed for the computation of the VBOs were obtained by the exact transformation of the {STRE, STRE, BEND} force fields, i.e. the forces on the CO stretching coordinates have been included during the transformation. Nevertheless, as advocated above, the resulting forces on the SPF coordinates have been neglected during the VBO calculations. If the forces are included in the representation of the PES or the SPF force field is transformed with the assumption of zero forces in the {STRE, STRE, BEND} representation, the

Table 6. Selected stretching force constants of N_2O computed at different levels of coupled-cluster theory.[a]

	cc-pVDZ			cc-pVTZ		
Force constant	CCSD	CCSDT	CCSDTQ	CCSD	CCSD(T)	CCSDT
f_r	0.1837	−0.3870	−0.4280	0.1445	−0.0313	−0.0801
f_R	−0.0860	−0.1530	−0.1671	0.0162	0.0006	−0.0592
f_{rr}	21.23	21.04	20.94	19.17	18.76	19.00
f_{RR}	13.11	13.98	13.43	12.06	12.33	12.38
f_{rrr}	−156.2	−155.6	−155.3	−143.4	−142.6	−142.6
f_{RRR}	−111.6	−109.9	−109.6	−102.6	−100.7	−101.1
f_{rrrr}	914.1	913.6	917.9	831.0	839.8	831.7
f_{RRRR}	658.1	658.2	659.6	606.9	605.0	606.2
f_{rrrrr}	−5198	−5210	−5190	−4836	−4812	−4842
f_{RRRRR}	−3358	−3546	−3567	−3138	−3367	−3308
f_{rrrrrr}	27025	28539	28404	31324	26961	31688
f_{RRRRRR}	24006	22607	21972	21798	19214	20607

[a] Units for the force constants are consistent with energy measured in attojoules and stretching coordinates (r and R) in angstroms. The force fields have been evaluated at the reference structure of $r(\mathrm{NN}) = 1.1273$ Å and $R(\mathrm{NO}) = 1.1851$ Å [46].

Table 7. Differences between vibrationally averaged and equilibrium rotational constants, in cm^{-1}, corresponding to ground and fundamental vibrational levels of $H_2{}^{16}O$.[a]

		Quadratic		Quartic		Sextic		
$(v_1\ v_2\ v_3)$		PAS	Eckart	PAS	Eckart	PAS	Eckart	Expt.
(0 0 0)	$\langle A\rangle_v - A_e$	1.8597	1.4440	0.9432	0.5536	0.8827	0.4910	0.4945
(0 0 0)	$\langle B\rangle_v - B_e$	0.0239	0.4395	−0.4455	−0.0560	−0.4715	−0.0798	−0.0588
(0 0 0)	$\langle C\rangle_v - C_e$	0.0304	0.0304	−0.2759	−0.2759	−0.2940	−0.2940	−0.2370
(0 0 0)	$\langle C_{\mathrm{Cor}}\rangle_v - C_e$		0.1097		−0.1998		−0.2178	−0.2370
(1 0 0)	$\langle A\rangle_v - A_e$	2.4814	2.0379	0.4371	0.0407	0.2084	−0.2008	
(1 0 0)	$\langle B\rangle_v - B_e$	0.2047	0.6481	−0.6183	−0.2219	−0.7026	−0.2934	
(1 0 0)	$\langle C\rangle_v - C_e$	0.1691	0.1691	−0.4069	−0.4069	−0.4684	−0.4684	
(1 0 0)	$\langle C_{\mathrm{Cor}}\rangle_v - C_e$		0.2531		−0.3311		−0.3921	
(0 1 0)	$\langle A\rangle_v - A_e$	4.4880	3.6207	4.4915	3.7561	4.5279	3.7930	
(0 1 0)	$\langle B\rangle_v - B_e$	0.0324	0.8996	−0.6225	0.1129	−0.6668	0.0681	
(0 1 0)	$\langle C\rangle_v - C_e$	−0.0067	−0.0067	−0.3260	−0.3260	−0.3462	−0.3462	
(0 1 0)	$\langle C_{\mathrm{Cor}}\rangle_v - C_e$		0.1846		−0.1389		−0.1584	
(0 0 1)	$\langle A\rangle_v - A_e$	2.8373	1.7719	0.5584	−0.4550	0.3208	−0.7077	
(0 0 1)	$\langle B\rangle_v - B_e$	−0.3702	0.6952	−1.1148	−0.1014	−1.2001	−0.1716	
(0 0 1)	$\langle C\rangle_v - C_e$	−0.0165	−0.0165	−0.5807	−0.5807	−0.6427	−0.6427	
(0 0 1)	$\langle C_{\mathrm{Cor}}\rangle_v - C_e$		0.1090		−0.4648		−0.5263	

[a] All results obtained from *ab initio* {STRE,STRE,BEND} force fields of different order [53]. See footnote [a] to table 1. PAS = rotational constants in principal axes system, Eckart = rotational constants in the Eckart frame. The equilibrium rotational constants corresponding to the reference geometry of the force field expansions are as follows: $A_e = 27.3154\,cm^{-1}$, $B_e = 14.5747\,cm^{-1}$, and $C_e = 9.5038\,cm^{-1}$. Experimental (Expt.) effective rotational constants were taken from [85]; the reported differences correspond to equilibrium rotational constants $A_e = 27.3861\,cm^{-1}$, $B_e = 14.5804\,cm^{-1}$, and $C_e = 9.5147\,cm^{-1}$, based on the final structure of [25].

Table 8. Differences between vibrationally averaged and equilibrium rotational constants, in $10^{-4}\,cm^{-1}$, corresponding to ground and fundamental vibrational levels of ${}^{12}C^{16}O_2$.[a]

		Quadratic		Quartic		Sextic		
$(v_1\ v_2\ v_3)$		PAS	Eckart	PAS	Eckart	PAS	Eckart	Expt.
(0 0 0)	$\langle B\rangle_v - B_e$	17.66	18.30	−13.21	−12.57	−13.55	−12.91	−14.19
(0 0 0)	$\langle C\rangle_v - C_e$	12.97	12.97	−17.85	−17.85	−18.19	−18.19	−14.19
(0 0 0)	$\langle C_{\mathrm{Cor}}\rangle_v - C_e$		18.30		−12.57		−12.91	−14.19
(1 0 0)	$\langle B\rangle_v - B_e$	40.42	41.07	−2.04	−1.39	−2.81	−2.16	−14.28
(1 0 0)	$\langle C\rangle_v - C_e$	29.27	29.27	−13.04	−13.04	−13.78	−13.78	−14.28
(1 0 0)	$\langle C_{\mathrm{Cor}}\rangle_v - C_e$		41.07		−1.39		−2.16	−14.28
(0 2 0)	$\langle B\rangle_v - B_e$	31.70	32.35	−14.86	−14.21	−15.52	−14.87	−11.53
(0 2 0)	$\langle C\rangle_v - C_e$	23.93	23.93	−22.48	−22.48	−23.17	−23.17	−11.53
(0 2 0)	$\langle C_{\mathrm{Cor}}\rangle_v - C_e$		32.35		−14.21		−14.87	−11.53
(0 0 1)	$\langle B\rangle_v - B_e$	16.48	18.41	−48.57	−46.67	−49.81	−47.90	
(0 0 1)	$\langle C\rangle_v - C_e$	11.77	11.77	−53.21	−53.21	−54.44	−54.44	
(0 0 1)	$\langle C_{\mathrm{Cor}}\rangle_v - C_e$		18.41		−46.67		−47.90	

[a] All results obtained from *ab initio* {STRE,STRE,BEND} force fields of different order [49]. See footnote [a] to table 2. PAS = rotational constants in principal axes system, Eckart = rotational constants in the Eckart frame. The equilibrium rotational constant corresponding to the reference geometry of the force field expansions is $B_e = C_e = 0.391623\,cm^{-1}$. Experimental (Expt.) effective rotational constants were taken from [86] and [52]; the reported differences correspond to the equilibrium rotational constant $B_e = C_e = 0.3916375\,cm^{-1}$ [86]. The larger than usual deviations between the sextic Eckart and the experimental results may be partially due to the strong resonance between the levels (1 0 0) and (0 2 0).

Table 9. Differences between vibrationally averaged and equilibrium rotational constants, in $10^{-4}\,\mathrm{cm}^{-1}$, corresponding to ground and fundamental vibrational levels of ${}^{14}N_2{}^{16}O$.[a]

		Quadratic		Quartic		Sextic		
$(v_1\ v_2\ v_3)$		PAS	Eckart	PAS	Eckart	PAS	Eckart	Expt.
(0 0 0)	$\langle B\rangle_v - B_e$	18.71	19.50	−20.13	−19.33	−20.56	−19.77	−21.42
(0 0 0)	$\langle C\rangle_v - C_e$	12.97	12.97	−25.84	−25.84	−26.27	−26.27	−21.42
(0 0 0)	$\langle C_{\mathrm{Cor}}\rangle_v - C_e$		19.50		−19.33		−19.77	−21.42
(1 0 0)	$\langle B\rangle_v - B_e$	31.43	32.32	−33.87	−32.97	−34.92	−34.02	−38.98
(1 0 0)	$\langle C\rangle_v - C_e$	23.07	23.07	−41.21	−41.21	−42.30	−42.30	−38.98
(1 0 0)	$\langle C_{\mathrm{Cor}}\rangle_v - C_e$		32.32		−32.97		−34.02	−38.98
(0 2 0)	$\langle B\rangle_v - B_e$	44.90	45.73	−6.49	−5.66	−7.51	−6.69	−12.32
(0 2 0)	$\langle C\rangle_v - C_e$	30.12	30.12	−22.10	−22.10	−23.04	−23.04	−12.32
(0 2 0)	$\langle C_{\mathrm{Cor}}\rangle_v - C_e$		45.73		−5.66		−6.69	−12.32
(0 0 1)	$\langle B\rangle_v - B_e$	17.48	19.77	−59.58	−57.32	−61.08	−58.82	−55.97
(0 0 1)	$\langle C\rangle_v - C_e$	11.72	11.72	−65.31	−65.31	−66.81	−66.81	−55.97
(0 0 1)	$\langle C_{\mathrm{Cor}}\rangle_v - C_e$		19.77		−57.32		−58.82	−55.97

[a] All results obtained from *ab initio* {STRE,STRE,BEND} force fields of different order [46]. See footnote [a] to table 4. PAS = rotational constants in principal axes system, Eckart = rotational constants in the Eckart frame. The equilibrium rotational constant corresponding to the reference geometry of the force field expansions is $B_e = C_e = 0.421113\,\mathrm{cm}^{-1}$. Experimental (Expt.) effective rotational constants were taken from [45] and [47]; the reported differences correspond to the equilibrium rotational constant $B_e = C_e = 0.421153\,\mathrm{cm}^{-1}$ [45].

STRE and SPF VBOs, both for the quartic and sextic representations, agree with each other to better than $0.5\,\mathrm{cm}^{-1}$.

Excellent agreement between experimental and computed VBOs can be seen for all empirical quartic and sextic force fields available for CO_2 and N_2O. While use of empirical quartic and sextic force fields result in a much better reproduction of experimental VBOs than that of *ab initio* force fields, it is clear that especially at higher (fifth- and sixth-) order the empirical force constants, obtained through different refinement procedures, do not correspond to the associated derivatives of the potential energy surface (PES).

Finally, it is necessary to comment on the apparent inaccuracy of the *ab initio* force fields of CO_2 and N_2O, which manifests in sizeable deviations between computed and experimental VBOs. While usually CCSD(T) theory gives highly accurate force constants [54], as can also be seen for H_2O in this study, for molecules with multiple bonds composed of highly electronegative atoms excitations larger than triples are necessary for the accurate characterization of the electronic structure. To prove this point, selected force constants have been recomputed for N_2O at the coupled-cluster hierarchy frozen-core cc-pVDZ CCSD, CCSDT, and CCSDTQ, and cc-pVTZ CCSD and CCSDT, employing the program MRCC [80] and the correlation-consistent (cc) basis sets of Dunning [79], with results presented in table 6.

4. Vibrationally averaged rotational constants

Vibrationally averaged effective rotational constants are the principal structural results obtained from fitting of appropriate rovibrational Hamiltonians to spectroscopic data. One can determine these constants from theoretical computations basically in two ways. The traditional route goes through VPT2 formulas [38–42] and the vibration–rotation interaction constants α obtained from a cubic force field expansion of the potential. The second route, employed in this study and preferred whenever it is feasible, computes the effective rotational constants as expectation values employing vibrational wavefunctions from variational calculations.

The rotational constants of triatomic molecules as functions of $\{R_1,R_2,\Theta\}$, which can be either Jacobi (Radau) or traditional {STRE, STRE, BEND} internal coordinates, can be obtained in two ways. First, one can set up the inertial tensor $\mathbf{I}$ in the principal axes coordinate system (PAS), in which case $\mathbf{I}$ is diagonal. Using PAS the rotational constant functions can simply be obtained as the inverse of the diagonal elements of $\mathbf{I}$. Second, the inertia tensor can be set up in the Eckart coordinate system, in which case the coordinates satisfy the Eckart conditions [72]. In this case the $\mathbf{I}$ matrix is not diagonal, and the rotational constant functions are derived from the diagonal matrix elements of the inverse of the $\mathbf{I}$ tensor neglecting the off-diagonal elements of $\mathbf{I}^{-1}$. Consideration of the Coriolis contribution results in a different **I** tensor but in the triatomic case only one of the rotational constants is changed [81].

The expectation values of the rotational constants of H_2O, CO_2, and N_2O in the ground and fundamental vibrational states [(0 2 0) instead of (0 1 0) for the linear molecules] are computed employing equation (7), and the wavefunctions correspond to the *ab initio* {STRE,STRE,BEND} representations of the PESs. In PAS the rotational constant functions were derived in {STRE,STRE,BEND} coordinates, while the rotational constant functions in the Eckart coordinate system were taken from [81], and they are functions of Jacobi coordinates. The calculated results are presented in tables 7–9.

One of the notable results of this study is that the agreement between the computed and experimental effective rotational constants is significantly better when the rotational constant functions employed refer to the Eckart and not the PAS coordinate system. Especially pronounced is the difference in case of the light H_2O molecule, where the results in PAS are much worse than in the Eckart frame. It is thus clear that the Eckart coordinates have to be employed to compute vibrationally averaged rotational constants as they have been employed in the derivation of the effective rovibrational Hamiltonians employed for the fitting of the experimental spectra. While some have realized this problem many years ago [81] there are cases where effective rotational constants have been computed in the PAS [82].

For the linear molecules, CO_2 and N_2O, the computed effective rotational constants are similar in the principle axes and Eckart coordinate systems. It is important to note that in all cases better agreement is obtained between computed and experimental data using the $C_{\mathrm{Cor}}(R_1,R_2,\Theta)$ rotational constant function [81]. The linear molecules have only one rotational constant, B, which is equal to C by symmetry. This holds neither in the PAS nor in the Eckart system when the Coriolis contribution is neglected. Therefore, a particularly important reason for including the Coriolis contribution in the expressions referring to the Eckart coordinate system is that only in this case will $\langle C_{\mathrm{Cor}}\rangle_{\boldsymbol{v}}$ of linear molecules be equal to $\langle B\rangle_{\boldsymbol{v}}$, where $\boldsymbol{v}$ represents vibrational quantum numbers.

5. Conclusions

One of the simplest possible technique for the variational solution of the nuclear motion Schrödinger equation results when the Hamiltonian is expanded in orthogonal (O) coordinates, its matrix is represented by the discrete variable representation (DVR) coupled with a direct product (P) basis, and advantage is taken of the sparsity of the resulting Hamiltonian matrix which can thus be diagonalized extremely efficiently by variants of sparse iterative (I) diagonalization techniques. The resulting procedure is termed DOPI for DVR – Hamiltonian in O coordinates – P basis – iterative (sparse Lanczos) diagonalization. The DOPI procedure has been programmed up and used exclusively during this study of triatomic systems.

The utility and applicability of force field expansions up to sextic terms for the variational computation of vibrational band origins (VBOs), deduced from results obtained for H_2O, CO_2, and N_2O, may be summarized as follows: (a) the remaining forces in the *ab initio* expansion of the potential should be neglected even in variational nuclear motion treatments; (b) the significant difference between VBOs obtained from quadratic and quartic force fields corresponding to STRE and SPF representations becomes insignificant when the full sextic force field is employed; (c) while use of empirical quartic and sextic force fields result in a much better reproduction of experimental VBOs than that of *ab initio* force fields, it is clear that especially at higher (fifth- and sixth-) order the empirical force constants, obtained through different refinement procedures, do not correspond to the associated derivatives of the potential energy surface (PES); and (d) numerical problems during the calculation of converged vibrational eigenvalues arise when full sextic force fields represent the potential but they can be dealt with if caution is exercised during the build-up of the Hamiltonian matrix.

The Eckart coordinates and not the principal axes coordinates have to be employed to compute vibrationally averaged rotational constants using variational vibrational wavefunctions, as only in this case can one compare meaningfully the first-principles effective rotational constants to their experimental counterparts. This is due to the fact that in the derivation of the effective rovibrational Hamiltonians used for the fitting of experimental spectra the Eckart coordinates have been employed. The resulting expressions must contain the Coriolis contribution as without this two different effective rotational constants are computed for linear molecules.

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Appendix

Analytic formulas for the transformation of internal coordinate force fields up to sextic terms from {STRE,

STRE, BEND} to {SPF, SPF, BEND} representation are given below. One can transform the complete sextic force field of triatomic molecules using the 15 explicit analytical formulas presented as the coefficients are the same in the formulas of different α-derivative SPF constants (*e.g.*, $f_{rr\alpha}^{\mathrm{SPF}} = r_{\mathrm{e}}^2 f_{rr\alpha} + 2r_{\mathrm{e}} f_{r\alpha}$ is obtained from $f_{rr}^{\mathrm{SPF}} = r_{\mathrm{e}}^2 f_{rr} + 2r_{\mathrm{e}} f_r$), while the r and r' coordinates can be inter-changed. In the notation employed f and f^{SPF} mean the force constant in {STRE,STRE,BEND} and {SPF,SPF,BEND} representations, respectively.

$$f_r^{\mathrm{SPF}} = r_{\mathrm{e}} f_r$$

$$f_{rr}^{\mathrm{SPF}} = r_{\mathrm{e}}^2 f_{rr} + 2r_{\mathrm{e}} f_r$$

$$f_{rr'}^{\mathrm{SPF}} = r_{\mathrm{e}} r'_{\mathrm{e}} f_{rr'}$$

$$f_{rrr}^{\mathrm{SPF}} = r_{\mathrm{e}}^3 f_{rrr} + 6r_{\mathrm{e}}^2 f_{rr} + 6r_{\mathrm{e}} f_r$$

$$f_{rrr'}^{\mathrm{SPF}} = r_{\mathrm{e}}^2 r'_{\mathrm{e}} f_{rrr'} + 2r_{\mathrm{e}} r'_{\mathrm{e}} f_{rr'}$$

$$f_{rrrr}^{\mathrm{SPF}} = r_{\mathrm{e}}^4 f_{rrrr} + 12r_{\mathrm{e}}^3 f_{rrr} + 36r_{\mathrm{e}}^2 f_{rr} + 24r_{\mathrm{e}} f_r$$

$$f_{rrrr'}^{\mathrm{SPF}} = r_{\mathrm{e}}^3 r'_{\mathrm{e}} f_{rrrr'} + 6r_{\mathrm{e}}^2 r'_{\mathrm{e}} f_{rrr'} + 6r_{\mathrm{e}} r'_{\mathrm{e}} f_{rr'}$$

$$f_{rrr'r'}^{\mathrm{SPF}} = r_{\mathrm{e}}^2 r'^2_{\mathrm{e}} f_{rrr'r'} + 2r_{\mathrm{e}} r'^2_{\mathrm{e}} f_{rr'r'} + 2r_{\mathrm{e}}^2 r'_{\mathrm{e}} f_{rrr'} + 4r_{\mathrm{e}} r'_{\mathrm{e}} f_{rr'}$$

$$f_{rrrrr}^{\mathrm{SPF}} = r_{\mathrm{e}}^5 f_{rrrrr} + 20r_{\mathrm{e}}^4 f_{rrrr} + 120r_{\mathrm{e}}^3 f_{rrr} + 240r_{\mathrm{e}}^2 f_{rr} + 120r_{\mathrm{e}} f_r$$

$$f_{rrrrr'}^{\mathrm{SPF}} = r_{\mathrm{e}}^4 r'_{\mathrm{e}} f_{rrrrr'} + 12r_{\mathrm{e}}^3 r'_{\mathrm{e}} f_{rrrr'} + 36r_{\mathrm{e}}^2 r'_{\mathrm{e}} f_{rrr'} + 24r_{\mathrm{e}} r'_{\mathrm{e}} f_{rr'}$$

$$\begin{aligned} f_{rrrr'r'}^{\mathrm{SPF}} = {} & r_{\mathrm{e}}^3 r'^2_{\mathrm{e}} f_{rrrr'r'} + 2r_{\mathrm{e}}^3 r'_{\mathrm{e}} f_{rrrr'} + 6r_{\mathrm{e}}^2 r'^2_{\mathrm{e}} f_{rrr'r'} \\ & + 12r_{\mathrm{e}}^2 r'_{\mathrm{e}} f_{rrr'} + 6r_{\mathrm{e}} r'^2_{\mathrm{e}} f_{rr'r'} + 12r_{\mathrm{e}} r'_{\mathrm{e}} f_{rr'} \end{aligned}$$

$$\begin{aligned} f_{rrrrrr}^{\mathrm{SPF}} = {} & r_{\mathrm{e}}^6 f_{rrrrrr} + 30r_{\mathrm{e}}^5 f_{rrrrr} + 300r_{\mathrm{e}}^4 f_{rrrr} + 1200r_{\mathrm{e}}^3 f_{rrr} \\ & + 1800r_{\mathrm{e}}^2 f_{rr} + 720r_{\mathrm{e}} f_r \end{aligned}$$

$$\begin{aligned} f_{rrrrrr'}^{\mathrm{SPF}} = {} & r_{\mathrm{e}}^5 r'_{\mathrm{e}} f_{rrrrr} + 20r_{\mathrm{e}}^4 r'_{\mathrm{e}} f_{rrrrr'} + 120r_{\mathrm{e}}^3 r'_{\mathrm{e}} f_{rrrr'} \\ & + 240r_{\mathrm{e}}^2 r'_{\mathrm{e}} f_{rrr'} + 120r_{\mathrm{e}} r'_{\mathrm{e}} f_{rr'} \end{aligned}$$

$$\begin{aligned} f_{rrrrr'r'}^{\mathrm{SPF}} = {} & r_{\mathrm{e}}^4 r'^2_{\mathrm{e}} f_{rrrrr'r'} + 2r_{\mathrm{e}}^4 r'_{\mathrm{e}} f_{rrrrr'} + 12r_{\mathrm{e}}^3 r'^2_{\mathrm{e}} f_{rrrr'r'} \\ & + 24r_{\mathrm{e}}^3 r'_{\mathrm{e}} f_{rrrr'} + 36r_{\mathrm{e}}^2 r'^2_{\mathrm{e}} f_{rrr'r'} + 72r_{\mathrm{e}}^2 r'_{\mathrm{e}} f_{rrr'} \\ & + 24r_{\mathrm{e}} r'^2_{\mathrm{e}} f_{rr'r'} + 48r_{\mathrm{e}} r'_{\mathrm{e}} f_{rr'} \end{aligned}$$

$$\begin{aligned} f_{rrrr'r'r'}^{\mathrm{SPF}} = {} & r_{\mathrm{e}}^3 r'^3_{\mathrm{e}} f_{rrrr'r'r'} + 6r_{\mathrm{e}}^3 r'^2_{\mathrm{e}} f_{rrrr'r'} + 6r_{\mathrm{e}}^2 r'^3_{\mathrm{e}} f_{rrr'r'r'} \\ & + 36r_{\mathrm{e}}^2 r'^2_{\mathrm{e}} f_{rrr'r'} + 6r_{\mathrm{e}}^3 r'_{\mathrm{e}} f_{rrrr'} + 6r_{\mathrm{e}} r'^3_{\mathrm{e}} f_{rr'r'r'} \\ & + 36r_{\mathrm{e}}^2 r'_{\mathrm{e}} f_{rrr'} + 36r_{\mathrm{e}} r'^2_{\mathrm{e}} f_{rr'r'} + 36r_{\mathrm{e}} r'_{\mathrm{e}} f_{rr'} \end{aligned}$$

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