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# Numerical-Analytic Implementation of the Higher-Order Canonical Van Vleck Perturbation Theory for the Interpretation of Medium-Sized Molecule Vibrational Spectra

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**ABSTRACT:** Anharmonic vibrational states of semirigid polyatomic molecules are often studied using the second-order vibrational perturbation theory (VPT2). For efficient higher-order analysis, an approach based on the canonical Van Vleck perturbation theory (CVPT), the Watson Hamiltonian and operators of creation and annihilation of vibrational quanta is employed. This method allows analysis of the convergence of perturbation theory and solves a number of theoretical problems of VPT2, e.g., yields anharmonic constants  $y_{ijk}$ ,  $z_{ijkl}$ , and allows the reliable evaluation of vibrational IR and Raman anharmonic intensities in the presence of resonances. Darling–Dennison and higher-order resonance coupling coefficients can be reliably evaluated as well. The method is illustrated on classic molecules: water and formaldehyde. A number of theoretical conclusions results, including the necessity of using sextic force field in the fourth order (CVPT4) and the nearly vanishing CVPT4 contributions for bending and wagging modes. The coefficients of perturbative Dunham-type Hamiltonians in high-orders of CVPT are found to conform to the rules of equality at different orders as earlier proven analytically for diatomic molecules. The method can serve as a good substitution of the more traditional VPT2.

$$H(p, q) = \sum_r \frac{\omega_r}{2} (q_r^2 + p_r^2) + V(q) \rightarrow \\ H(a^+, a) = \sum_r \omega_r \left( a_r^+ a_r + \frac{1}{2} \right) + V(a^+, a) \\ \hat{H}_k^{(k)} = \hat{H}_k^{(k-1)} + i[S_k, H_0]$$

## 1. INTRODUCTION

Vibrational spectroscopy benefits from quantum-mechanical methods for predicting the frequencies of vibrational transitions and their probabilities with an accuracy of fractions of a percent, allowing reliable assignment of observed transitions.<sup>1–6</sup> Within the Born–Oppenheimer approximation, the general rovibronic problem splits into purely electronic and vibrational parts for a nonrotating molecule. Therefore, a two-stage procedure suffices for the theoretical prediction of vibrational frequencies and intensities. The link between these stages is the molecular potential energy surface (PES) and the dipole moment surface (DMS), obtained quantum-mechanically. Once the PES and the DMS are available, the further solution of the vibrational Schrödinger equation can be accomplished by either the variational method or the vibrational perturbation theory in one of their forms.

Although the solution of the electronic Schrödinger equation is a more sophisticated problem than solution of the vibrational one, there is a shortage of comprehensive methods and software for the latter problem using, in particular, perturbation theory. As noticed in ref 7, “general computer codes improving on the harmonic oscillator approximation and able to treat a polyatomic molecule of an arbitrary type are still scarce and far from enjoying the popularity of the electronic-oriented packages”. A variety of program codes<sup>7–15</sup> that go beyond the crude harmonic oscillator–rigid rotor model utilize either the perturbation theory approach, mainly in the second-order of vibrational perturbation theory (VPT2), or the variational method. The variational method<sup>14,16</sup> is usually applicable to small molecules (5–7 atoms). A simplified version of it is called the vibrational self-consistent field (VSCF) method,<sup>17,18</sup> which is essentially a vibrational analogue of the corresponding

electronic technique and applicable to molecules of much larger size (~30 atoms).

VPT2 allows efficient calculation of frequencies and intensities of fundamentals and other types of vibrational transitions of large molecules, using closed expressions<sup>2–5,19–26</sup> for anharmonic constants and resonance coupling coefficients, usually employing the reduced quartic force field. VPT2 is typically used in a black-box manner, without a critical analysis of the underlying theory and possible peculiarities in the implementation. At the same time, modern advances in computational quantum chemistry allow obtaining more accurate force fields than quartic (e.g., sextic), while available theoretical techniques and computer power permit not only implementation of VPT2 in a more thorough way, but work with higher orders of perturbation theory.

In a wider context, there are some fundamental problems of molecular structure and spectroscopy that could be addressed by more accurate implementation of perturbation theory. For example, our knowledge of the molecular PES characteristics and their spectroscopic manifestations is rather modest beyond diatomic molecules. It is also very important to know which molecular internal degrees of freedom are associated with a large-amplitude motion and what are the spectroscopic manifestations of such effects. To answer these types of questions, it is necessary to be able to accurately predict highly excited vibrational states of molecules, which need the calculation of higher-order anharmonic constants  $y_{ijk}$ ,  $z_{ijkl}$ , etc. that are not available through VPT2.

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Although a quartic polynomial expansion of the potential has a limited radius of convergence, VPT2 can produce a very accurate description of anharmonic vibrational states. The classical one-dimensional Morse potential<sup>27</sup> provides a good description of potential curves of diatomic molecules due to a correct asymptotic behavior. Nevertheless, despite the qualitative difference between these potentials, the exact eigenvalues of the vibrational Schrödinger equation using the Morse potential coincide with the VPT2 eigenvalues for the polynomial quartic potential, obtained directly from Morse function by differentiation.<sup>28,29</sup> This fact justifies using VPT2 for polyatomic molecules, especially organic molecules containing C–H bonds, for which the anharmonic correction is of the order of 150 cm<sup>-1</sup>. However, for *a priori* non-Morse internal degrees of freedom (like bending, wagging etc.), the above effect is not necessarily the case, which leaves open the question of the importance of contributions to the potential higher than quartic.

VPT2 provides analytical expressions for anharmonic constants and resonance coupling terms that can be obtained using either Rayleigh–Schrödinger perturbation theory (RSPT)<sup>4,30–32</sup> or canonical Van Vleck perturbation theory (CVPT).<sup>33,2,4,5,19–22</sup> CVPT is a very powerful theoretical tool for molecular spectroscopy. It is based on a series of algebraic unitary canonical (contact) transformations of the Hamiltonian expressed in operator form. Since the fundamental work of Nielsen and co-workers,<sup>19–21</sup> CVPT analysis has been accomplished using the coordinate-momentum representation. The operators defining the first and second canonical transformations ( $S_1$  and  $S_2$ ) were deduced in the analytical form,<sup>21,34–38</sup> which allowed not only obtaining anharmonic constants (for which only  $S_1$  is needed) but also evaluating the analytic expressions for the fundamental transition matrix elements and infrared intensities after transforming the dipole moment operator using both  $S_1$  and  $S_2$ .<sup>26,31,39–47</sup> Already for the second contact transformation, the  $S_2$  operators become cumbersome in the CVPT formalism,<sup>36</sup> and, to the best of our knowledge, the form of operators  $S_3$ ,  $S_4$  was never obtained.

In 1961 Primas<sup>48,49</sup> formulated CVPT using a superoperator formalism in the domain of Lie algebra. In 1970, Birss and Choi<sup>50</sup> suggested that CVPT can be accomplished in a Fock representation, i.e. using creation and annihilation operators (CAO). This representation provides a dual advantage. First, obtaining  $S$  operators in the Fock representation is trivial,<sup>23,50,51</sup> contrary to the quite involved procedure in coordinate-momentum representation.<sup>23,37,38,52,53</sup> Second, any vibrational resonance can be expressed in concise and comprehensive form using CAO product.

From the mid-1970s, the group of Makushkin and co-workers<sup>23,54</sup> combined the above ideas and presented a number of papers and monographs on a thorough study of superoperator formulation of CVPT in the CAO representation. This group also wrote a Fortran program for performing vibration–rotational CVPT for a diatomic molecule in symbolic form.<sup>54</sup>

In 1988, Sibert<sup>55</sup> summarized the earlier developments of CVPT and implemented them in the program VANVLK,<sup>11</sup> using the Meyer–Günthard–Pickett (MGP) Hamiltonian<sup>56–58</sup> and CAO representation. Comparing results obtained for some molecules by CVPT and the variational method, Pak, Sibert, and Woods found that “the fourth order results ... are often essentially exact”.<sup>59</sup> Although the very convincing works of Sibert and co-workers (e.g., refs 11, 55, and 59–65) are extensively quoted in the literature, to the best of our

knowledge there are no further independent systematic works based on Sibert’s approach.

Recently CVPT methods were developed by several other groups. For example, in 2002, Joyeux and Sugny published a survey<sup>66</sup> on CVPT advocating its advantages and suggesting its use in cases of floppy molecules and molecules with internal rotation. In 2008 Lamouroux et al.<sup>67</sup> developed an advanced program MOL\_CT that is able to perform CVPT for a triatomic molecule in purely analytic or mixed numerical-analytic forms and can include rotational effects.

As shown by McCoy and Sibert,<sup>62,63</sup> the CVPT transformations for a polyatomic molecule can be efficiently formalized as a computer algorithm if the Hamiltonian in original and reduced forms is expressed using CAO products with numerical floating point aggregate coefficients, what can be called the numerical-analytic CVPT. The central feature of this approach is using the MGP Hamiltonian in curvilinear normal coordinates that are linear combinations of genuine curvilinear valence coordinates. The advantages of this approach are as follows: (a) anharmonicity is distributed between the kinetic and potential energy operators; (b) better modeling of wide-amplitude internal motion; and (c) faster convergence of CVPT and better description of highly excited states. However, implementation of this approach requires expanding the kinetic energy operator in sixth order power series using a numerical differentiation technique. Besides, the potential must be converted to the representation in the curvilinear coordinates, a formidable task beyond the quartic form.<sup>68,69</sup>

From the theoretical point of view, the results obtained with MGP or Watson<sup>70</sup> Hamiltonians must be identical, although MGP Hamiltonian ensures better convergence for highly excited states. For molecules of bigger size than four to five atomics, however, the density of highly excited states substantially hinders both experimental and theoretical studies.

This article is devoted to numerical-analytic implementation of CVPT using the CAO representation for the Watson Hamiltonian in a similar way as it is fulfilled in works of Sibert and co-workers.<sup>11,55,59–65</sup> Employing the Watson Hamiltonian simplifies the method for several reasons: (a) the kinetic energy and Coriolis coupling operators are converted to CAO representation in exact form; (b) the potential energy expansion coefficients in rectilinear normal coordinates can be obtained from the Cartesian force field by a linear transformation. In the second order, this approach produces the same results as customary VPT2, assuming the latter is employed in a comprehensive manner without omissions. However, correct accounting of the second-order Darling–Dennison resonances can not be performed within a VPT2 that employs analytical expressions because the terms for coupling coefficients contain resonance denominators themselves.<sup>71,72</sup>

A possibility of applying CVPT at orders higher than second (which seems to be impossible in the traditional form of closed expressions) would answer some very important questions, such as the analysis of convergence of CVPT expansions<sup>73</sup> and its improvement by careful treatment of resonance interactions. In our study, we also aimed at applicability of this method to polyatomic molecules of larger size than it was achieved by Sibert et al.<sup>11,55,59–65</sup>

Vibrational transitions can be very dense even for medium sized molecules. Thus, being able to predict vibrational transitions of all types could be a great aid to making correct assignments of experimental observations. Although the differences between intensities of fundamental transitions

evaluated in double-harmonic and anharmonic approximations are not typically significant, a resonance effect can cause a redistribution of intensities by orders of magnitude. Therefore, it is important to do a thorough accounting of the resonances. VPT2 allows evaluation of anharmonic intensities, but this is a complicated method,<sup>26</sup> requiring very careful treatment of Fermi and Darling–Dennison resonances. The numerical-analytic CVPT handles this problem in an efficient and straightforward way.

The importance of further development of theory and accurate and efficient application of CVPT for many aspects of vibrational spectroscopy justifies a detailed step-by-step review of existing theoretical foundations of the method as it helps a wider circle of researchers understand the whole picture with practical tools for implementing advanced versions of perturbation theory.

The outline of the current paper is as follows. In sections 2 and 3 we consider the model Hamiltonian, the vibrational Schrödinger equation and the application of CVPT for its solution. Section 4 is devoted to CAO formalism applied to the anharmonic problem. The vibrational resonances are considered in section 5. Evaluation of spectroscopic parameters and energy levels is described in section 6, while evaluation of intensities is outlined in section 7. The computer-specific issues are tackled in section 8. The examples and discussion are given in section 9, followed by the Conclusions (section 10).

## 2. MODEL HAMILTONIAN AND VIBRATIONAL SCHRÖDINGER EQUATION

For the anharmonic vibrational analysis of a polyatomic molecule, it is customary<sup>22</sup> to expand a model Hamiltonian  $H = T + V$  in powers of rectilinear dimensionless normal coordinates  $q_r = (4\pi^2 c \omega_r / h)^{1/2} Q_r$ , where  $\omega_r$  is a harmonic frequency and  $Q_r$  is Wilson's normal coordinate.<sup>1</sup> In the standard case, the potential energy operator  $V$  is limited to the second order (quartic force field)

$$\begin{aligned} V &= V_0 + V_1 + V_2 \\ &= \frac{1}{2} \sum_r \omega_r q_r^2 + \frac{1}{6} \sum_r \sum_s \sum_t \phi_{rst} q_r q_s q_t \\ &\quad + \frac{1}{24} \sum_r \sum_s \sum_t \sum_u \phi_{rstu} q_r q_s q_t q_u \end{aligned} \quad (2.1)$$

The kinetic energy operator<sup>70</sup> is then expressed using the conjugated momenta  $p_r = -i(\partial/\partial q_r)$ , and the Coriolis coupling operators  $\pi_\alpha$  at the zero eigenvalue of the rotational operator ( $J = 0$ )

$$\begin{aligned} T &= T_0 + T_2 = \frac{1}{2} \sum_r \omega_r p_r^2 + \sum_{\alpha=x,y,z} B_e^\alpha \pi_\alpha^2, \\ \pi_\alpha &= \sum_r \sum_s \zeta_{rs}^\alpha \left( \frac{\omega_s}{\omega_r} \right)^{1/2} q_r p_s \end{aligned} \quad (2.2)$$

Here equilibrium rotational constants are designated as  $B_e^\alpha$  and Coriolis coupling constants are designated as  $\zeta_{rs}^\alpha$ . The summation in 2.1 is performed over all of vibrational degrees of

freedom,  $M$ . To simplify the formalism, we shall only deal with nondegenerate modes. The total Hamiltonian  $H = T + V$  grouped by orders of perturbation theory has the following form,

$$\begin{aligned} H &= T + V \\ &= \left[ \frac{1}{2} \sum_r \omega_r (p_r^2 + q_r^2) \right] + \left[ \frac{1}{6} \sum_r \sum_s \sum_t \phi_{rst} q_r q_s q_t \right] \\ &\quad + \left[ \frac{1}{24} \sum_r \sum_s \sum_t \sum_u \phi_{rstu} q_r q_s q_t q_u \right] \\ &\quad + \sum_{\alpha=x,y,z} B_e^\alpha \left( \sum_{r \neq s} \sum_{t \neq u} \zeta_{rs}^\alpha \zeta_{tu}^\alpha \left( \frac{\omega_s}{\omega_r} \right)^{1/2} \left( \frac{\omega_u}{\omega_t} \right)^{1/2} q_r p_s q_t p_u \right) \end{aligned} \quad (2.3)$$

where  $\phi_{rst}$  etc. are force constants (in  $\text{cm}^{-1}$  units) expressed in dimensionless normal coordinates.

With the Hamiltonian 2.3, the vibrational Schrödinger equation

$$H\Psi = E\Psi \quad (2.4)$$

may not be solved analytically, but an approximate solution is possible through perturbation theory<sup>19–22</sup> with the assumption that the required eigenvalues of the vibrational Schrödinger eq 2.4 are smooth functions of the Hamiltonian parameters  $\omega_r$ ,  $\phi_{rst}$ ,  $\phi_{rstu}$ ,  $B_e^\alpha$ ,  $\zeta_{rs}^\alpha$ . The eigenvalues in eq 2.4 can be expanded in a Taylor series in powers of matrix elements,  $\langle \Psi_0 | ((p_r^2 + q_r^2)/2) | \Psi_0 \rangle = \nu_r + 1/2$

$$\begin{aligned} E(hc)^{-1} &= E_0 + \sum_r \omega_r \left( \nu_r + \frac{1}{2} \right) + \sum_{r \leq s} x_{rs} \left( \nu_r + \frac{1}{2} \right) \left( \nu_s + \frac{1}{2} \right) \\ &\quad + \sum_{r \leq s \leq t} y_{rst} \left( \nu_r + \frac{1}{2} \right) \left( \nu_s + \frac{1}{2} \right) \left( \nu_t + \frac{1}{2} \right) \\ &\quad + \sum_{r \leq s \leq t \leq u} z_{rstu} \left( \nu_r + \frac{1}{2} \right) \left( \nu_s + \frac{1}{2} \right) \left( \nu_t + \frac{1}{2} \right) \left( \nu_u + \frac{1}{2} \right) + \dots \end{aligned} \quad (2.5)$$

The expansion 2.5 is a generalization of Dunham's empirical expansion of vibration–rotation energy of a diatomic molecule<sup>74</sup> for the case of a polyatomic molecule in the absence of rotation. It is well documented that parameters  $\omega_r$ ,  $x_{rs}$  in eq 2.5 may be efficiently obtained by fitting energy levels to observed peaks in spectrum with the typical residual discrepancy of a few wavenumbers. Such fitting serves as a solid justification of the Dunham-type series 2.5 truncation at the second order.

The efficiency of perturbation theory can be attributed to two circumstances. First, the second-order vibrational perturbation theory (VPT2) expansion coefficients in 2.5 can be obtained in closed form as functions of the Hamiltonian parameters  $\omega_r$ ,  $\phi_{rst}$

$\phi_{rstu}$ ,  $B_e^\alpha$ ,  $\zeta_{rs}^\alpha$  using either customary Rayleigh–Schrödinger or canonical Van Vleck versions of the perturbation theory:<sup>4,5,19–22</sup>

$$x_{rr} = \frac{1}{16}\phi_{rrrr} - \frac{1}{32} \sum_{s=1}^M \phi_{rrs}^2 \left[ \frac{1}{2\omega_r + \omega_s} - \frac{1}{2\omega_r - \omega_s} + \frac{4}{\omega_s} \right] \quad (2.6)$$

$$x_{rs} = \frac{1}{4}\phi_{rrss} - \frac{1}{4} \sum_t \frac{\phi_{rrt}\phi_{tss}}{\omega_t} + \sum_{\alpha=x,y,z} B_e^\alpha (\zeta_{rs}^\alpha)^2 \left[ \frac{\omega_r}{\omega_s} + \frac{\omega_s}{\omega_r} \right] - \frac{1}{8} \sum_t \phi_{rst}^2 \left[ \frac{1}{\omega_r + \omega_s + \omega_t} + \frac{1}{-\omega_r + \omega_s + \omega_t} + \frac{1}{\omega_r - \omega_s + \omega_t} - \frac{1}{\omega_r + \omega_s - \omega_t} \right] \quad (2.7)$$

Through these expressions the phenomenological spectroscopic constants  $\omega_r$ ,  $x_{rs}$ , ..., obtained by fitting them to observed transitions, gain physical meaning. Second, and this is a key advantage of the perturbation theory, applying VPT2 to a Morse potential yields the exact eigenvalues.<sup>28,29</sup>

In the second order (VPT2), the perturbation theory does not answer the important question about convergence of the Dunham expansion 2.5. Concerning the other limitations of VPT2, it is evident from formulas 2.6 and 2.7 that quartic force constants of the type  $\phi_{ijij}$ ,  $\phi_{ijkj}$ ,  $\phi_{ijkl}$  have no effect on the anharmonic constants  $x_{ij}$ . Such force constants only affect higher-order anharmonic force constants  $y_{ijk}$ ,  $z_{ijkl}$ , ... in 2.5. In fact, force constants  $\phi_{ijij}$ ,  $\phi_{ijkj}$ ,  $\phi_{ijkl}$  contribute to Darling–Dennison resonance coupling coefficients  $K_{DD}$ ,<sup>32,71,72,75–79</sup> but they may also give nonresonance higher-order contributions to the vibrational energy. There are several types of coefficients  $K_{DD}$  and obtaining correct analytic expressions for them requires “extensive algebra”.<sup>32,71,72,75–79</sup> Besides, analytical formulas<sup>32,71,72,75–79</sup> for  $K_{DD}$  may themselves contain resonance denominators, e.g.,

$$K_{rrss} = \frac{1}{4}\phi_{rrss} - \sum_{\alpha=x,y,z} B_e^\alpha (\zeta_{rs}^\alpha)^2 \frac{(\omega_r + \omega_s)^2}{\omega_r \omega_s} - \frac{1}{8} \sum_k \phi_{krr}\phi_{kss}\omega_k \left( \frac{1}{\omega_k^2 - 4\omega_r^2} + \frac{1}{\omega_k^2 - 4\omega_s^2} \right) - \frac{1}{2} \sum_k \phi_{krs}^2 \frac{\omega_k}{\omega_k^2 - (\omega_r - \omega_s)^2} \quad (2.8)$$

As stated in ref 72, “the perturbation theory model does not produce reliable Darling–Dennison constants owing to small denominators” in equations of the type of eq 2.8. The terms with small denominators can be dropped off,<sup>77,71</sup> which means that the corresponding interactions are treated as the first-order resonances. The ordinary scheme of implementing VPT2,<sup>80</sup> as is employed in Gaussian 03<sup>13</sup> uses the “semidiagonal” quartic force field ( $\phi_{ijkl} = 0$ ), so that some types of  $K_{DD}$  constants are omitted.

### 3. CANONICAL VAN VLECK PERTURBATION THEORY (CVPT)

In this section, we will briefly outline the CVPT basics and present the general formula for unitary canonical (contact) transformations without specifying the method of obtaining the transformation operators. In CVPT, the original Hamiltonian  $H$  in an algebraic operator form is subjected to a sequence of  $k$  canonical transformations  $U = U_k \dots U_2 U_1$ , that gradually reduce  $H$  to the special form desired,  $\hat{H}$ . These transformations leave the spectrum of eigenvalues of  $\hat{H}$  intact,

$$\hat{H}\hat{\Psi} \equiv UHU^{-1}\hat{\Psi} = E\hat{\Psi} \quad (3.1)$$

but modify the wave functions

$$\hat{\Psi} = U\Psi, \quad \Psi = U^{-1}\hat{\Psi} \quad (3.2)$$

Each unitary transformation is defined in the exponential form proposed by van Vleck,<sup>33,81</sup>

$$U_k = \exp(iS_k), \quad U_k^{-1}U_k = I \quad (3.3)$$

where a Hermitian operator  $S_k$  is called the generator of a unitary transformation. The exponential form 3.3 of  $U_k$  is typically used in an expanded form:

$$U_k = \exp(iS_k) = 1 + iS_k - \frac{1}{2}S_k^2 - i\frac{1}{6}S_k^3 + \dots = \sum_{n=0}^{\infty} \frac{i^n}{n!} S_k^n \quad (3.4)$$

The series of unitary transformations,  $U_1$ ,  $U_2$ , ...,  $U_k$ , gradually reduces  $H$  to  $\hat{H}$  in such a way that the following commutation conditions are fulfilled ( $[A, B] = AB - BA$ ),

$$[\hat{H}_k, H_0] = 0 \quad (3.5)$$

Here  $H_0$  is the Hamiltonian of a zero-order vibrational problem. In our case it has the form:

$$H_0 = \frac{1}{2} \sum_r \omega_r (q_r^2 + p_r^2) \quad (3.6)$$

The solution of the classical zero-order Schrödinger equation

$$H_0\Psi_0 = E_0\Psi_0 \quad (3.7)$$

is available in closed form.<sup>1,4</sup> The commutation property 3.5 ensures that both zero-order Hamiltonian and transformed full Hamiltonian 2.3 have a common system of eigenfunctions. Fulfillment of this condition provides a solution of the problem: the knowledge of the explicit form of transformed Hamiltonian and its eigenfunctions  $\Psi_0$  reduces the eigenvalue determination to a trivial task of the evaluation of diagonal matrix elements:

$$E_i = \langle (\Psi_0)_i | \hat{H} | (\Psi_0)_i \rangle \quad (3.8)$$

The remaining questions are as follows: (a) the choice of operators  $S_1$ ,  $S_2$ , ...,  $S_k$ , defining particular unitary transformations, and (b) the method of evaluation of the transformed Hamiltonian,  $\hat{H} = UHU^{-1}$ . The latter transformation is readily accomplished by the Campbell–Hausdorff formula,

$$\hat{H} = H + i[S, H] - \frac{1}{2!}[S, [S, H]] - \frac{i}{6}[S, [S, [S, H]]] + \dots = H + \sum_{n=1}^{\infty} \frac{(i)^n}{n!} \underbrace{[S, [S, \dots [S, H] \dots]]}_n \quad (3.9)$$



Table 1. General Scheme of Canonical Van Vleck Transformations of the Hamiltonian<sup>a</sup>

order	$H_0$	$H_1$	$H_2$	unitary transformation
0	$\hat{H}_0^{(0)} = U_0 H_0 U_0^{-1}$	$\hat{H}_1^{(0)} = U_0 H_1 U_0^{-1}$	$\hat{H}_2^{(0)} = U_0 H_2 U_0^{-1}$	$U_0 = 1$
1	—	$\hat{H}_1^{(1)} = U_1 \hat{H}_1^{(0)} U_1^{-1}$	$\hat{H}_2^{(1)} = U_1 \hat{H}_2^{(0)} U_1^{-1}$	$U_1 = 1 + iS_1$
2	—	—	$\hat{H}_2^{(2)} = U_2 \hat{H}_2^{(1)} U_2^{-1}$	$U_2 = 1 + iS_2 - (1/2)S_2^2$

<sup>a</sup>The original Hamiltonian is given by expansion 3.10 by orders of perturbation theory, unitary transformations  $U$  are given by expansion 3.4, and the transformed Hamiltonian term  $\hat{H}_n^{(K)}$  is defined by the general formula 3.11.

The determination of transformation operators  $S_1, S_2, \dots, S_k$  will be discussed in the next section. In general, they can be obtained by solving an appropriate system of linear equations.<sup>38,52,53</sup>

The representation of the overall unitary transformation  $U$  as the product of  $U_k$  operators,  $U = U_K \dots U_2 U_1$ , is essential for the step-by-step reduction of the Hamiltonian to the desired form by orders of perturbation theory. This allows truncating the infinite expansion 3.9 for each transformation in an appropriate way. In brief, a perturbation theory parameter  $\lambda$  is introduced, which varies from zero to unity, corresponding to the zero-order and fully perturbed problems, accordingly. Then, the original Hamiltonian 2.3 is expanded by orders of a perturbation theory, multiplying terms by increasing powers of the parameter  $\lambda$ :

$$H = H_0 + \sum_{k=1}^K \lambda^k H_k \quad (3.10)$$

Cooper<sup>28</sup> made an observation that in the case of Morse Hamiltonian the quantity  $x_e^{1/2}$ , where  $x_e = (h\omega)/(8\pi D_e)$ , acts as a natural perturbation parameter. The parameter  $\lambda$  is also introduced into unitary transformations,  $U_k(\lambda) = \exp(i\lambda^k S_k)$ . Rewriting all the equations with the parameter  $\lambda$  included, collecting terms and equating parts with like powers of  $\lambda$ , one obtains the following general expression for the Hamiltonian, subjected to  $K$  sequential unitary transformations,  $\hat{H}^{(K)}$ ,<sup>19–23,66,82,83</sup>

$$\hat{H}_k^{(K)} = \hat{H}_k^{(K-1)} + \sum_{m=0}^{l-1} \frac{i^{l-m}}{(l-m)!} [S_K, [S_K, \dots [S_K, \hat{H}_{k+m+L}^{(K-1)}] \dots], \quad (3.11)$$

where  $l = (k - L)/K$  and  $L = \text{mod}(k, K)$  is the remainder of division of  $k$  by  $K$ . Transformation operators  $S_K$  are evaluated from the following equations of the general form:

$$\hat{H}_K^{(K)} = \hat{H}_K^{(K-1)} + i[S_K, H_0] \quad (3.12)$$

where  $S_K$  is chosen in such a way that  $\hat{H}_K^{(K)}$  takes the desired (quasi-)diagonal form. In the absence of resonances this condition is equivalent to the requirement that  $\hat{H}_K^{(K)}$  commutes with  $H_0$ :

$$[\hat{H}_K^{(K)}, H_0] = 0. \quad (3.13)$$

It should be noted that in case of resonances the condition 3.13 will have a slightly different form.

The fully transformed Hamiltonian  $\hat{H}^{(K)}$  is obtained via summation:

$$\hat{H}^{(K)} = H_0 + \sum_{k=1}^K \hat{H}_k^{(K)} \quad (3.14)$$

In general, the overall scheme of canonical transformations can be conveniently represented as in Table 1, which clearly

shows what terms of the Hamiltonian of different orders are subjected to particular transformations, and what parts of operator series are used accordingly.

For example, applying 3.11 up to the second order, the transformed Hamiltonian takes the following form:

$$\begin{aligned} \hat{H}^{(2)} = & H_0 + H_1 + i[S_1, H_0] + H_2 + i[S_1, H_1] \\ & - \frac{1}{2}[S_1, [S_1, H_0]] + i[S_2, H_0] \end{aligned} \quad (3.15)$$

#### 4. CREATION/ANNIHILATION OPERATORS AND THE ANHARMONIC PROBLEM

The idea of formulating CVPT in terms of creation and annihilation operators (also called second quantization or Fock representation) was put forward in 1970 by Birss and Choi,<sup>50</sup> and developed in refs 23, 51, 84, and 85. A number of good reviews are also available.<sup>86,87</sup>

The creation and annihilation operators (CAO) of vibrational quanta are defined as follows,

$$a^+ = \frac{1}{\sqrt{2}}(q - ip), \quad a = \frac{1}{\sqrt{2}}(q + ip) \quad (4.1)$$

The transformation from coordinate-momentum representation to CAO representation can be accomplished via the inverse expressions,

$$q = \frac{1}{\sqrt{2}}(a^+ + a), \quad p = \frac{1}{\sqrt{2}}i(a^+ - a) \quad (4.2)$$

In the case of a multidimensional problem each pair of CAO's has a separate index corresponding to a particular degree of freedom, and operators with different indices commute.

Acting on a zero-order (harmonic) vibrational wave function, CAO increases or decreases vibrational quantum numbers, for this reason they are also called ladder or rising/lowering operators,

$$a^+|v\rangle = \sqrt{v+1}|v+1\rangle, \quad a|v\rangle = \sqrt{v}|v-1\rangle \quad (4.3)$$

Different products of CAO can be equivalent; i.e., they can produce the same result acting on wave functions. This relationship explains why there are several ordering schemes,<sup>23</sup> of which so-called normal ordering is commonly used in CVPT. For the normal ordering, CAO are arranged in such a way that the power of creation operator is put on the left side and the power of the annihilation operator is put on the right side:  $(a^+)^m (a)^n$ . An arbitrary product of CAO can be readily

reduced to the normal form by applying the following formula recursively,<sup>55</sup>

$$(a^+)^k a^l (a^+)^m (a)^n = (a^+)^{k+m} (a)^{l+n} + \sum_{i=1}^{\min(l,m)} \left[ \frac{1}{i!} \prod_{j=0}^{i-1} (l-j)(m-j) \right] (a^+)^{k+m-i} (a)^{l+n-i} \quad (4.4)$$

As was already stated in the Introduction, the application of CAO provides two significant advantages that make the implementation of CVPT and the description of vibrational resonances straightforward. In the next section, we will consider vibrational resonances in detail, but first we will see how application of CAO affects the CVPT formalism and simplifies the evaluation of  $S_1$ ,  $S_2$ , ...,  $S_k$ .

The Hamiltonian  $H$  2.3 should first be rewritten in CAO using definition 4.2. For example, the harmonic Hamiltonian 3.6 has the following form:

$$H_0 = \frac{1}{2} \sum_r \omega_r (q_r^2 + p_r^2) = \frac{1}{2} \sum_r \omega_r (2a_r^+ a_r + 1) \quad (4.5)$$

In principle, transformation of the full anharmonic Hamiltonian  $H$  eq 2.3 to the CAO representation can be done by merely substituting eq 4.2 into eq 2.3, opening brackets and collecting like terms, but such an operation would produce too many terms of different kinds and handling them is impractical even with the help of computer algebra systems. Instead, it is convenient to rewrite parts of  $H$  in such a way that coordinate/momentum products are grouped by the same type of reduction to the normal form, eq 4.4. Appropriate forms of terms  $V_1$  and  $V_2$  in eq 2.1 are as follows:

$$V_1 = \frac{1}{6} \left[ \sum_{r=1}^M \phi_{rrr} q_r^3 + 3 \sum_{r=1}^{M-1} \sum_{s=r+1}^M (\phi_{rrs} q_r^2 q_s + \phi_{rss} q_r q_s^2) + 6 \sum_{r=1}^{M-2} \sum_{s=r+1}^{M-1} \sum_{t=s+1}^M \phi_{rst} q_r q_s q_t \right] \quad (4.6)$$

$$V_2 = \frac{1}{24} \left[ \sum_{r=1}^M \phi_{rrrr} q_r^4 + 6 \sum_{r=1}^{M-1} \sum_{s=r+1}^M \phi_{rrss} q_r^2 q_s^2 + 4 \sum_{r=1}^{M-1} \sum_{s=r+1}^M (\phi_{rrrs} q_r^3 q_s + \phi_{rsss} q_r q_s^3) + 12 \sum_{r=1}^{M-2} \sum_{s=r+1}^{M-1} \sum_{t=s+1}^M (\phi_{rrst} q_r^2 q_s q_t + \phi_{rsst} q_r q_s^2 q_t + \phi_{rstt} q_r q_s q_t^2) + 24 \sum_{r=1}^{M-3} \sum_{s=r+1}^{M-2} \sum_{t=s+1}^{M-1} \sum_{u=t+1}^M \phi_{rstu} q_r q_s q_t q_u \right] \quad (4.7)$$

The second-order kinetic energy term  $T_2$  acquires the form

$$T_2 = -\frac{1}{4} \sum_{\alpha=x,y,z} B_e^\alpha \left( \sum_{r \neq s} \sum_{t \neq u} \zeta_{rs}^\alpha \zeta_{tu}^\alpha (\omega_s \omega_u / (\omega_r \omega_t))^{1/2} \Theta_{rstu} \right) \quad (4.8)$$

where

$$\begin{aligned} \Theta_{rstu} = & a_r^+ a_s^+ a_t^+ a_u^+ - a_r^+ a_s^+ a_t^+ a_u + a_r^+ a_s^+ a_t a_u^+ \\ & - a_r^+ a_s^+ a_t a_u - a_r^+ a_s a_t^+ a_u^+ + a_r^+ a_s a_t^+ a_u \\ & - a_r^+ a_s a_t a_u^+ + a_r^+ a_s a_t a_u + a_r a_s^+ a_t^+ a_u^+ \\ & - a_r a_s^+ a_t^+ a_u + a_r a_s^+ a_t a_u^+ - a_r a_s^+ a_t a_u \\ & - a_r a_s a_t^+ a_u^+ + a_r a_s a_t^+ a_u - a_r a_s a_t a_u^+ + a_r a_s a_t a_u \end{aligned} \quad (4.9)$$

Furthermore, individual terms in 4.9 must be reduced to the normal form using 4.4.

When the full Hamiltonian  $H$  in eq 2.3 is expressed using CAO, the general CVPT formula 3.11 can be applied up to any desired order. To accomplish that, it is also necessary to know the explicit forms of operators  $S_1$ ,  $S_2$ , ...,  $S_k$  and a practical method of the commutator evaluation.

Probably the main advantage of CAO is the possibility of deriving transformation operator  $S_k$  directly from  $\hat{H}_K^{(K-1)}$  using a trivial formula, which was proposed by Birss and Choi.<sup>50</sup> Once the Hamiltonian  $\hat{H}_K^{(K-1)}$  is expressed as a sum of normalized operator terms,

$$\hat{H}_K^{(K-1)} = \sum_j h_j \prod_{l=1}^M (a_l^+)^{m_{jl}} (a_l)^{n_{jl}} \quad (4.10)$$

and the diagonal terms with equal powers ( $m_{jl} = n_{jl}$ ) are removed from 4.10, the corresponding transformation operator  $S_K$  is immediately derived using the simple formula,<sup>23,50</sup>

$$S_K = -i \sum_j h_j \left( \sum_{l=1}^M (m_{jl} - n_{jl}) \omega_l \right)^{-1} \prod_{l=1}^M (a_l^+)^{m_{jl}} (a_l)^{n_{jl}} \quad (4.11)$$

Simplicity of the formula 4.11 is a consequence of a commutation relation,<sup>51</sup>

$$\begin{aligned} & [i((a^+)^m (a)^n - (a^+)^n (a)^m), H_0] \\ & = -i(m - n) \omega ((a^+)^m (a)^n + (a^+)^n (a)^m) \end{aligned} \quad (4.12)$$

This property ensures that solution of eq 3.12 and eq 3.13 for a transformation operator  $S_K$  is reduced to a system of linear equations with a diagonal matrix.<sup>51</sup>

Here we have considered the idealized nonresonance case, assuming that the denominators in 4.11 are not vanishing. The theory of resonances will be dealt with in the next section.

Once transformation operators  $S_K$  are known and available in a form similar to 4.11 for accomplishing sequential unitary transformations 3.11, it is necessary to be able to evaluate nested commutators of the type:  $[S_K, [S_K, \dots [S_K, H] \dots]]$ .

As suggested by Sibert,<sup>55</sup> evaluation of a simple commutator  $[S_K H]$  is equivalent to evaluation of the following expression,

$$[S_K, H] = \sum_k \sum_j s_k h_j \prod_{r=1}^M [ (a_r^+)^{m_{kr}} (a_r)^{n_{kr}} (a_r^+)^{m_{jr}} (a_r)^{n_{jr}} - (a_r^+)^{m_{jr}} (a_r)^{n_{jr}} (a_r^+)^{m_{kr}} (a_r)^{n_{kr}} ] \quad (4.13)$$

by reduction of terms to the normal form using 4.4 and subsequent collection of terms in a resulting operator polynomial. Nested commutators are evaluated sequentially.

## 5. VIBRATIONAL RESONANCES

From the quantum mechanical point of view, a vibrational resonance can be unequivocally represented by the following operator  $F$  using CAO, so that the aggregate frequency determined by all creation operators approximately equals to the frequency determined by all annihilation operators,

$$F = f \prod_{l=1}^M (a_l^+)^{m_l} (a_l)^{n_l}, \quad \sum_{l=1}^M m_l \omega_l \approx \sum_{l=1}^M n_l \omega_l \quad (5.1)$$

In the framework of CVPT, the resonances manifest themselves by the appearance of terms with abnormally big coefficients in  $S$  operators what results in divergent perturbative expansions in eq 2.5. It is evident from eq 4.11, that the numerical coefficients of the following structure,

$$\Omega_k = h_k \left( \sum_{l=1}^M (m_{kl} - n_{kl}) \omega_l \right)^{-1} \quad (5.2)$$

are responsible for resonances as they become abnormally big in absolute value. The total power of CAO in a resonance operator  $F$  in eq 5.1 may not be higher than the order of CVPT + 2. The first order resonances are called Fermi ones, and the second order ones are Darling–Dennison resonances.

The usual procedure of working with resonances is as follows.<sup>11,66</sup> At the stage of defining the transformation operator  $S_K$  using eq 4.11, those terms of the original Hamiltonian that produce  $|\Omega_k|$  coefficients bigger than certain chosen cutoff parameter  $\Omega_{cutoff}$  are ignored and they do not contribute to  $S_K$ . As a result, the transformed Hamiltonian  $\hat{H}_K^{(K)}$ , eq 3.12, will contain not only diagonal terms that commute with  $H_0$ , but also those resonance terms that were excluded from formation of  $S_K$ . Eventually, the fully transformed Hamiltonian  $\hat{H}^{(K)}$  in eq 3.14 will contain certain number of nondiagonal terms that are treated by matrix diagonalization.

As mentioned by Joyeux and Sugny,<sup>66</sup> “it is not necessarily the resonances with the smallest value of  $\sum_j (m_j - n_j) \omega_j$  that prove to be important, but instead those with the largest values of  $\Omega_k$ ”. It is clear from 5.2 that coefficients  $\Omega_k$  are dimensionless which makes the criterion for choosing resonances more universal than commonly used in VPT2 criteria in terms of a separation in  $\text{cm}^{-1}$ .<sup>88</sup> The appropriate value of cutoff parameter as a resonance condition  $|\Omega_k| > \Omega_{cutoff}$  can be chosen by comparing “good” terms in  $S_K$  with abnormal ones. For example, in the case of the  $\text{H}_2\text{O}$  molecule, for Fermi resonance  $\omega_1 \approx 2\omega_2$  the parameter  $\Omega_k$  equals to  $\sim 0.1$ , and for Darling–Dennison resonance  $2\omega_1 \approx 2\omega_3$  it equals  $\sim 0.2$ . A significant advantage of CVPT procedures for treatment of resonances vs commonly used VPT2 schemes<sup>88</sup> is that the same resonance criterion  $|\Omega_k| > \Omega_{cutoff}$  can be applied at any order of CVPT.

To illustrate the limitations of the traditional method of the treatment of resonances, it is necessary to recall certain features of the customary VPT2 procedure. According to Papoušek and Aliev’s fundamental monograph,<sup>22</sup> analytic expressions for anharmonic constants are obtained from diagonal matrix elements of the Hamiltonian, subjected to a single canonical transformation. It means that what is called VPT2 is in fact a combination of single CVPT contact transformation followed by the first-order Rayleigh–Schrödinger perturbation theory (RSPT) step. In principle, for a nondegenerate case, anharmonic constants can be obtained by second-order RSPT without any involvement of transformation operators  $S$ .<sup>4</sup> Generally speaking, the evaluation of anharmonic constants and the second-order Darling–Dennison resonance coefficients must be synchronized with careful removal of the first-order resonances. The first-order CVPT step in customary VPT2 ensures that all Fermi first-order resonances are carefully detected and corresponding off-diagonal matrix elements are calculated using<sup>89</sup>

$$W_{ij} = \langle v_i + 2, v_j | f_{ij} (a_i^+)^2 (a_j) | v_i, v_j + 1 \rangle = f_{ij} \left( \frac{(v_i + 2)(v_i + 1)(v_j + 1)}{32} \right)^{1/2} \quad (5.3)$$

$$W_{ijk} = \langle v_i + 1, v_j + 1, v_k | f_{ijk} (a_i^+) (a_j^+) (a_k) | v_i, v_j, v_k + 1 \rangle = f_{ijk} \left( \frac{(v_i + 1)(v_j + 1)(v_k + 1)}{8} \right)^{1/2} \quad (5.4)$$

Accounting for the second-order Darling–Dennison resonances in VPT2 framework must be done manually by calculating several types of coupling coefficients  $K_{DD}^{32,71,72,75-79}$  with subsequent matrix diagonalization. For this purpose it is also necessary to know anharmonic force constants of the  $\phi_{rstu}$  type, which are not always available, for example, in the Gaussian 03 implementation of VPT2.<sup>13,80</sup>

The limitations of VPT2 are highlighted in the calculation of anharmonic intensities of fundamental bands.<sup>26,40-47,83</sup> This procedure requires the explicit form of the second-order transformation operators  $S_1, S_2$  that are used for canonical transformation of the dipole moment or the polarizability operators.<sup>46,47,83</sup> Because of mixing of resonating states, the intensities distribute between “bright” and “dark” states, and this effect is controlled by values of corresponding resonance coupling constants. Therefore, it is vital to synchronize removal of resonance terms from  $S_1, S_2$  with the evaluation of these coupling couplings.

Let us consider the variational part in more detail. The Hamiltonian matrix in the basis of zero-order (harmonic) wave functions  $\Psi_0 \equiv |v_1, v_2, v_3, \dots, v_M\rangle$  is infinite and composed of matrix elements of all possible pairs of  $\Psi_0(v_i^A)$  and  $\Psi_0(v_i^B)$ , characterized by quantum numbers. It is easy to verify that the only nonvanishing matrix element  $X_{A,B}$  of a single nondiagonal Hamiltonian term of the type

$$F = f \prod_{l=1}^M (a_l^+)^{m_l} (a_l)^{n_l} \quad (5.5)$$



is given by the following expression, where  $k_l = m_l - n_l$ :

$$\begin{aligned} X_{A,B} &= \langle \Psi_0(v_l^A) | F | \Psi_0(v_l^B) \rangle \\ &= \langle v_1 + k_1, v_2 + k_2, \dots, v_M + k_M | F | v_1, v_2, \dots, v_M \rangle \end{aligned} \quad (5.6)$$

Among the numbers  $k_l$  there are both positive and negative values, otherwise no resonance takes place. Substituting in 5.6 all possible combinations of quantum numbers with the only requirement  $v_l + k_l \geq 0$ , one obtains an infinite number of matrix elements that will differ by numerical coefficients arising from multipliers in 4.3. It is convenient to re-express 5.6 in equivalent form in order to move all negative values of  $k_l$  to the right side,

$$\begin{aligned} &\langle \Psi_0(v_l^A) | F | \Psi_0(v_l^B) \rangle \\ &= \prod_{l(k_l > 0)}^M (\langle v_l + k_l | F | v_l \rangle) \prod_{l(k_l < 0)}^M (\langle v_l - k_l | \rangle) \end{aligned} \quad (5.7)$$

All nondiagonal Hamiltonian terms have Hermitian-conjugate pairs, so that the resulting Hamiltonian matrix is a Hermitian one. In practice, for a polyatomic molecule it is necessary to restrict the number of basis functions, say, to the number corresponding to total excitation of 2, 3, or 4. The choice of the basis functions for such a procedure is discussed in ref 64.

## 6. SPECTROSCOPIC PARAMETERS AND VIBRATIONAL STATES

In this section, we consider how the canonically transformed Hamiltonian is converted to the perturbative representation utilizing the sets of spectroscopic constants and what differences appear when going from the second to higher (even) orders of CVPT.

**6.1. Second Order CVPT (CVPT2).** After two successive contact transformations, the initial Hamiltonian  $H$  gains the new form,  $\hat{H}^{(2)} = \hat{H}_D + \hat{H}_R$ . The first, “diagonal” part,  $\hat{H}_D$ , contains only operators, that produce nonzero matrix elements on the main diagonal of Hamiltonian matrix in the zero-order basis. The second “resonance” part,  $\hat{H}_R$ , conversely produce nonzero matrix elements only off the main diagonal. The general expression for  $\hat{H}^{(2)}$ , fully reduced to normal form, is therefore given by

$$\begin{aligned} \hat{H}^{(2)} &= \hat{H}_D + \hat{H}_R \\ &= \sum_k d_k \prod_{l=1}^M (a_l^+)^{m_{kl}} (a_l)^{n_{kl}} \\ &\quad + \sum_j f_j \prod_{l=1}^M (a_l^+)^{m_{jl}} (a_l)^{n_{jl}} \end{aligned} \quad (6.1)$$

where the total power of each operator product is limited to four in the second order. The diagonal part of the Hamiltonian  $\hat{H}_D$  makes the major contribution to the vibrational energy, while the resonance part  $\hat{H}_R$  must be treated separately by means of numerical diagonalization of the finite block of the

Hamiltonian matrix in the appropriately chosen basis of zero-order wave functions.

It is convenient to use the notation of the number operator  $N \equiv a^+ a$ . The eigenvalue of  $N$  for the zero-order eigenfunction  $\Psi_0(v)$  is its quantum number,  $N \Psi_0(v) = v \Psi_0(v)$ . The “power” of the number operator is accordingly defined by:

$$N^{[n]} \equiv (a^+)^n (a)^n = N(N-1)(N-2)\dots(N-n+1) \quad (6.2)$$

with eigenvalues

$$N^{[n]} \Psi_0(v) = v(v-1)(v-2)\dots(v-n+1) \Psi_0(v) \quad (6.3)$$

Such a definition of the “power” of the number operator is chosen for the reason that  $N^{[n]}$  is always reduced to the normal form, unlike  $N^n \equiv (a^+ a)^n$ . Using the number operator notation, the second-order diagonal Hamiltonian  $\hat{H}_D^{(2)}$  can be rewritten as follows:

$$\begin{aligned} \hat{H}_D^{(2)} &= d_0 + \sum_{i=1}^M d_i N_i + \sum_{i=1}^M d_{ii} N_i^{[2]} \\ &\quad + \sum_{i=1}^{M-1} \sum_{j=i+1}^M d_{ij} N_i N_j \end{aligned} \quad (6.4)$$

As operators  $N_i$  for different modes commute, the double summation in eq 6.4 is limited, i.e. the following double indexation rule is obeyed:  $i < j$ . Evidently,  $\hat{H}_D^{(2)}$  in the form 6.4 commutes with  $H_0$ , and this property ensures that the wave functions  $\Psi_0(v)$  are also eigenfunctions of  $\hat{H}_D^{(2)}$ .

The general form of diagonal matrix element of  $\hat{H}_D^{(2)}$  in the basis of zero-order wave functions is obtained trivially from eq 6.4 using the property 6.3,

$$\begin{aligned} &\langle \prod_{i=1}^M \Psi_0(v_i) | \hat{H}_D^{(2)} | \prod_{i=1}^M \Psi_0(v_i) \rangle \\ &= d_0 + \sum_{i=1}^M d_i v_i + \sum_{i=1}^M d_{ii} v_i (v_i - 1) \\ &\quad + \sum_{i=1}^{M-1} \sum_{j=i+1}^M d_{ij} v_i v_j \end{aligned} \quad (6.5)$$

This formula for the second-order vibrational energy  $E^{(2)}$  as a function of the set of quantum numbers ( $v_1, v_2, \dots, v_M$ ) can be further re-expressed in the Dunham-type form:

$$\begin{aligned} E^{(2)}(v_1, v_2, \dots, v_M) \\ &= E_0 + \sum_{i=1}^M \omega_i \left( v_i + \frac{1}{2} \right) + \sum_{i=1}^M x_{ii} \left( v_i + \frac{1}{2} \right)^2 \\ &\quad + \sum_{i=1}^{M-1} \sum_{j=i+1}^M x_{ij} \left( v_i + \frac{1}{2} \right) \left( v_j + \frac{1}{2} \right) \end{aligned} \quad (6.6)$$

The equality  $1/2(p_i^2 + q_i^2) = a_i^+ a_i + 1/2$  explains why the expansion 6.6 of vibrational energy has the customary form in powers of  $(v_i + 1/2)$  instead of pure quantum numbers  $v_i$ .

It is straightforward to show that quantities  $E_0$ ,  $\omega_i$ ,  $x_{ii}$ ,  $x_{ij}$  can be expressed in terms of parameters of the diagonal Hamiltonian  $\hat{H}_D^{(2)}$  as follows:

$$E_0 = d_0 - \frac{1}{2} \sum_{i=1}^M \left( d_i - \frac{3}{2} d_{ii} \right) + \frac{1}{4} \sum_{i=1}^{M-1} \sum_{j=i+1}^M d_{ij} \quad (6.7)$$

$$\omega_i = d_i - 2d_{ii} - \frac{1}{2} \sum_{j=1}^M d_{ij} \quad (6.8)$$

$$x_{ii} = d_{ii}, x_{ij} = d_{ij} \quad (6.9)$$

It should be noted that  $E_0$  coincides with Dunham parameter  $Y(0,0)$  and  $d_0$  is what is usually called a zero-point energy (ZPE).

The final expression for fundamental frequencies can be obtained from eq 6.6:

$$\begin{aligned} \nu_i &= E^{(2)}(0, 0, \dots, \nu_i = 1, \dots, 0) - E^{(2)}(0, 0, \dots, 0) \\ &= \omega_i + 2x_{ii} + \frac{1}{2} \sum_{j=1, j \neq i}^M x_{ij} \end{aligned} \quad (6.10)$$

The expressions for overtones and combination bands can be easily obtained in the same way.

It can be proven by the direct consideration of matrix elements of 6.5 corresponding to  $i$ th fundamental vibrational energy state that they include only the first-order terms  $d_0$ ,  $d_i$

$$\left\langle \prod_{l=1}^M \Psi_0(\nu_l = 0, \nu_i = 1) \right| \hat{H}_D^{(2)} \left| \prod_{l=1}^M \Psi_0(\nu_l = 0, \nu_i = 1) \right\rangle = d_0 + d_i \quad (6.11)$$

so that fundamental frequencies  $\nu_i$  simply coincide with  $d_i$ . The same result can be obtained by comparing eqs 6.8, 6.9, and 6.10.

The above analytical treatment is only related to  $\hat{H}_D^{(2)}$ , the diagonal part of  $\hat{H}^{(2)}$ , and all values of vibrational levels evaluated so far are usually called “deperturbed”, as all resonance interactions have been excluded at this stage. The solution for the fully transformed Hamiltonian  $\hat{H}^{(2)} = \hat{H}_D^{(2)} + \hat{H}_R^{(2)}$  is further obtained variationally via diagonalization of a Hamiltonian matrix written in the zero-order basis. The main diagonal of this matrix is composed of the values of vibrational levels obtained by formulas of 6.10 type. Off-diagonal matrix elements are calculated trivially,

$$\begin{aligned} &\left\langle \prod_{l=1}^M \Psi_0^A(\nu_l) \right| \hat{H}_R^{(2)} \left| \prod_{l=1}^M \Psi_0^B(\nu_l) \right\rangle \\ &= \sum_j f_j \prod_{l=1}^M \langle \Psi_0^A(\nu_l) | (a_l^+)^{m_{jl}} (a_l)^{n_{jl}} | \Psi_0^B(\nu_l) \rangle \end{aligned} \quad (6.12)$$

In certain cases (smaller molecules with few resonances) the Hamiltonian matrix may take a block-diagonal form,<sup>61</sup> and the exact solution is therefore obtained by numerical diagonalization. Generally, the Hamiltonian matrix has quasi-diagonal structure, and it is a good approximation to truncate it at low levels of vibrational excitation, with total quanta equal to 2, 3, or 4.

When it is possible to choose the canonical transformation in such a way, so that the Hamiltonian becomes block-diagonal, it is very convenient to describe these small-size blocks in terms of the so-called polyad numbers.<sup>63,90–92</sup> From the physical point of view, the block-diagonal structure of the Hamiltonian means an appearance of an additional constant of motion besides the total energy.<sup>91</sup> The key fact is that “one needs to find only one additional constant of motion other than energy in order to transform to a block diagonal Hamiltonian”.<sup>63</sup> The presence of several polyad numbers, which is often the case, breaks down the block-diagonal structure of the Hamiltonian.<sup>92</sup> In larger molecules with a bigger number of resonances, especially in higher orders, the choice of polyad quantum number(s) is ambiguous. An expert user can take advantage of the flexibility of CVPT and choose the set of allowed resonances in such a way that there is only one polyad number left and the Hamiltonian becomes block-diagonal. This is not always possible, and each molecule must be considered individually.

Let us consider in detail the structure of  $\hat{H}_R^{(2)}$  with regard to CVPT orders. This evaluation is important because the structure of the first-order resonances is repeated in the odd orders with the distinction that the first-order resonance operator is multiplied by increasing powers of number operators, which allows representation of this family of resonances by a special form of a power series.<sup>66</sup>

The first-order Fermi resonances are defined by the two possible types of operators (in all instances below, the Hermitian conjugate component must be added):

$$F_{ii,j}^{(1)} = (a_i^+)^2 (a_j), \quad F_{ij,k}^{(1)} = (a_i^+) (a_j^+) (a_k) \quad (6.13)$$

In the second order, the Darling–Dennison resonances are associated with the following operators:

$$F_{ii,jj}^{(2)} = (a_i^+)^2 (a_j)^2, \quad F_{ii,jk}^{(2)} = (a_i^+)^2 (a_j) (a_k), \quad F_{ij,kl}^{(2)} = (a_i^+) (a_j^+) (a_k) (a_l) \quad (6.14a)$$

$$F_{i,j}^{(2)} = (a_i^+) (a_j), \quad F_{ii,ij}^{(2)} = (a_i^+) N_i (a_j), \quad F_{ij,jk}^{(2)} = (a_i^+) N_j (a_k) \quad (6.14b)$$

$$F_{i,jjk}^{(2)} = (a_i^+) (a_j)^2 (a_k), \quad F_{i,jkl}^{(2)} = (a_i^+) (a_j) (a_k) (a_l) \quad (6.14c)$$

It should be noted that operators in eq 6.14c above define the three-quanta transitions.

**6.2. Fourth and Higher Orders of CVPT.** For the fourth-order CVPT (CVPT4), the initial Hamiltonian  $H$  is subjected to four successive contact transformations, and it takes the similar general form as for CVPT2, but the total power of each operator product with the same index is limited to six versus four in case of CVPT2:

$$\begin{aligned} \hat{H}^{(4)} &= \hat{H}_D^{(4)} + \hat{H}_R^{(4)} \\ &= \sum_k d_k \prod_{l=1}^M (a_l^+)^{m_{kl}} (a_l)^{m_{kj}} \\ &\quad + \sum_j f_j \prod_{l=1}^M (a_l^+)^{m_{jl}} (a_l)^{n_{jl}} \end{aligned} \quad (6.15)$$

Using the number operator notation, the fourth-order Hamiltonian  $\hat{H}_D^{(4)}$  takes the following form:

$$\begin{aligned} \hat{H}_D^{(4)} = & d_0 + \sum_{i=1}^M d_i N_i + \sum_{i=1}^M d_{ii} N_i^{[2]} \\ & + \sum_{i=1}^{M-1} \sum_{j=i+1}^M d_{ij} N_i N_j + \sum_{i=1}^M d_{iii} N_i^{[3]} \\ & + \sum_{i=1}^{M-1} \sum_{j=i+1}^M d_{ijj} N_i^{[2]} N_j + \sum_{i=1}^{M-1} \sum_{j=i+1}^M d_{ijj} N_i N_j^{[2]} \\ & + \sum_{i=1}^{M-2} \sum_{j=i+1}^{M-1} \sum_{k=j+1}^M d_{ijk} N_i N_j N_k \end{aligned} \quad (6.16)$$

The representation 6.16 can be converted to the Dunham form analytically with some effort. Using Maplesoft Maple, we have obtained the necessary formulas, but they are more cumbersome than eqs 6.7–6.9 and therefore causing the risk of introducing errors while transferring formulas to Fortran increases.

We have found that a simple numerical procedure does the same job for CVPT4 and for any higher orders of CVPT in uniform style. For this purpose, the eigenvalue of  $N^{[n]}$  (eq 6.3) must be rewritten in an equivalent form using the definition  $u = v + 1/2$ :

$$\begin{aligned} & v(v-1)(v-2)\dots(v-n+1) \\ & = \left(u - \frac{1}{2}\right)\left(u - \frac{3}{2}\right)\left(u - \frac{5}{2}\right)\dots\left(u - n + \frac{1}{2}\right) \end{aligned} \quad (6.17)$$

Taking the diagonal matrix element of  $\hat{H}_D^{(4)}$  from eq 6.16 in zero-order wave functions using eq 6.3, making the substitution eq 6.17, opening brackets and finally collecting the terms with like powers of  $u$ , solves the problem. Substituting  $u = v + 1/2$  into the resulting expression yields the desired Dunham form of the CVPT4 vibrational energy:

$$\begin{aligned} E^{(4)}(v_1, v_2, \dots, v_M) \\ = E_0 + \sum_i \omega_i \left(v_i + \frac{1}{2}\right) + \sum_{i \leq j} x_{ij} \left(v_i + \frac{1}{2}\right) \left(v_j + \frac{1}{2}\right) \\ + \sum_{i \leq j \leq k} y_{ijk} \left(v_i + \frac{1}{2}\right) \left(v_j + \frac{1}{2}\right) \left(v_k + \frac{1}{2}\right) \end{aligned} \quad (6.18)$$

Subsequently, obtaining the expression for fundamental frequencies from the constants  $E_0$ ,  $\omega_i$ ,  $x_{ij}$ ,  $y_{ijk}$  from eq 6.18 is very similar to the procedure outlined above for CVPT2.

The structure of resonance operators in third and fourth orders ( $K = 3, 4$ ) is similar to the ones in lower orders. The structure of individual resonance operators in eq 6.15 is given by:

$$F^{(K)} = f \prod_{l=1}^M (a_l^+)^{m_l} (a_l)^{n_l}, \quad \sum_{l=1}^M (m_l + n_l) = K + 2 \quad (6.19)$$

An essential feature of higher-order resonances ( $K > 2$ ) is that a lower order resonance operator is multiplied by powers

of the number operator; for instance, a Fermi resonance operator transforms,

$$\begin{aligned} F_{ii,j}^{(1)} = f_{ii,j}^{(1)} (a_i^+)^2 (a_j) & \rightarrow F_{ii,j}^{(3)} = f_{ii,j}^{(3)} (a_i^+)^2 (a_j) (a_k^+ a_k) \\ \text{or } F_{ii,j}^{(3)} = f_{ii,j}^{(3)} (a_i^+)^2 (a_j)^2 & \end{aligned} \quad (6.20)$$

A very similar situation is encountered for the second-order Darling–Dennison resonances.

A family of resonance operators of the same basic structure that are gradually accumulated in the off-diagonal part of higher-order transformed Hamiltonian  $\hat{H}_R^{(K)}$  may be given by,<sup>66</sup>

$$\begin{aligned} F_{(K)} = & \prod_{l=1}^M (a_l^+)^{m_l} \{f_0^{(K)} + \sum_{j=1}^M f_j^{(K)} N_j + \dots \\ & + \sum_{j=1}^M \sum_{k=j}^M \dots f_{jk\dots}^{(K)} N_j N_k \dots\} \prod_{l=1}^M (a_l)^{n_l} \end{aligned} \quad (6.21)$$

where the number of single/multiple summations (including  $f_0^{(K)}$ ) in curly brackets is equal to  $K/2$ . The off-diagonal matrix element  $X_{A,B}^{(K)}$  of the operator  $F^{(K)}$  is given by (compare with eq 6.12):

$$\begin{aligned} X_{A,B}^{(K)} = & \langle \prod_{l=1}^M \Psi_0(v_l^A) | F^{(K)} | \prod_{l=1}^M \Psi_0(v_l^B) \rangle \\ = & \left( \prod_{l=1}^M C_l^{(m_l)} \right) \langle \prod_{l=1}^M \Psi_0(v_l^A + m_l) | \\ & \{f_0^{(K)} + \sum_{j=1}^M f_j^{(K)} N_j + \dots \\ & + \sum_{j=1}^M \sum_{k=j}^M \dots f_{jk\dots}^{(K)} N_j N_k \dots\} \left( \prod_{l=1}^M C_l^{(n_l)} \right) \\ & | \prod_{l=1}^M \Psi_0(v_l^B - n_l) \rangle \end{aligned} \quad (6.22)$$

Hermitian conjugate parts of  $F^{(K)}$  produce symmetric matrix elements over the main diagonal; they are omitted here. The multipliers  $C_l^{(m_l)}$ ,  $C_l^{(n_l)}$  appear due to CAO operators acting on wave functions

$$C_l^{(m_l)} = \prod_{k=1}^{m_l} \sqrt{v_l^A + k}, \quad C_l^{(n_l)} = \prod_{k=1}^{n_l} \sqrt{v_l^B - k + 1} \quad (6.23)$$

It is distinctly seen from eq 6.21 which of the particular matrix elements will be nonzero. As the number operators in curly brackets do not alter quantum numbers, the condition of obtaining a nonzero matrix element is meeting the following relationship for the sets of quantum numbers  $v_l^A$ ,  $v_l^B$ ,

$$(v_l^A + m_l) = (v_l^B - n_l) = v_l \geq 0 \quad (6.24)$$

in view of basis function orthogonality. Finally, the resonance matrix element is given by

$$X_{A,B}^{(K)} = \left( \prod_{l=1}^M C_l^{(m_l)} C_l^{(n_l)} \right) \{ f_0^{(K)} + \sum_{j=1}^M f_j^{(K)} v_j + \dots + \sum_{j=1}^M \sum_{k=j}^M \dots f_{jk}^{(K)} v_j v_k \dots \} \quad (6.25)$$

where the set of quantum numbers  $v_l$  is defined by relationship 6.24. Therefore, sets of coupling coefficients for resonances of each kind can be conveniently represented in a general form similar to the Dunham expansion. From 6.25, it is seen that the number of nonzero matrix elements for each type of resonance interaction is formally infinite and only restricted by the dissociation limit. In practice the maximum level of excitation must be chosen in view of the problem to be solved. The expression 6.25 is very useful for establishing the relationship between empirically found resonance coupling coefficients for different levels of excitation.

## 7. EVALUATION OF INTENSITIES

If an analytical form of the  $S$ -functions is known, one can find a representation of an arbitrary operator  $\Xi$  of a physical quantity (given by its Taylor expansion) in a basis of zero-order functions  $\Psi_0$ , and, consequently, obtain analytical formulas for matrix elements, corresponding to observable quantities:

$$\begin{aligned} \langle \Phi^{(a)} | \Xi | \Phi^{(b)} \rangle &= \langle (U^{-1} \Phi_0^{(a)}) | \Xi | U^{-1} \Phi_0^{(b)} \rangle \\ &= \langle \Phi_0^{(a)} | U \Xi U^{-1} | \Phi_0^{(b)} \rangle \end{aligned} \quad (7.1)$$

For the Boltzmann distribution of molecules at absolute temperature  $T$  the integral absorption coefficient of electric dipole moment transition  $a \leftarrow b$  is given by the following formula:<sup>5,93</sup>

$$\begin{aligned} I^{(ab)} &= \int \varepsilon(\nu) d\nu \\ &= \frac{8\pi^3 N_A}{3hcQ} \nu^{(ab)} S^{(ab)} [e^{-E^{(b)}/kT} - e^{-E^{(a)}/kT}] \end{aligned} \quad (7.2)$$

where  $N_A$  is the Avogadro's number,  $k$  is the Boltzmann's constant,  $\nu^{(ab)}$  is the transition wavenumber, and  $Q$  is the partition function. The eq 7.2 contains the line strength of the electric dipole transition,

$$S^{(ab)} = \sum_{\alpha} |\langle \Psi^{(a)} | M_{\alpha} | \Psi^{(b)} \rangle|^2 \quad (7.3)$$

where  $\Psi^{(a)}$  and  $\Psi^{(b)}$  are full wave functions, corresponding to the nondegenerate eigenstates  $E^{(a)}$  and  $E^{(b)}$ , while  $M_{\alpha}$  is the  $\alpha$  component of the molecular dipole moment operator in the space-fixed coordinate system ( $\alpha = X, Y, Z$ ). The quantum-mechanical expression for operator  $M_{\alpha}$  coincides with the classical expression for the dipole moment function,

$$M_{\alpha} = e \sum_{i=1}^m Z_i \bar{r}_i - e \sum_{k=1}^n \bar{r}_k \quad (7.4)$$

where  $e$  is the elementary charge,  $Z_i$  is the charge of  $i$ th nucleus, and  $\bar{r}_i, \bar{r}_k$  are  $\alpha$  components of coordinates of  $i$ th nucleus and  $k$ th electron, respectively. Within the Born–Oppenheimer

approximation, the wave function of the molecule is represented by a product of the electronic wave function and the nuclear one that allows an independent integration with respect to coordinates of electrons and nuclei for the evaluation of matrix elements 7.3. In this case eq 7.3 is reduced to

$$S^{(ab)} = \sum_{\alpha} |\langle \Phi^{(a)} | \sum_{\beta} \varphi_{\alpha\beta} \mu_{\alpha}(q) | \Phi^{(b)} \rangle|^2 \quad (7.5)$$

where  $\Phi^{(a)}, \Phi^{(b)}$  are the vibration–rotation wave functions,  $\varphi_{\alpha\beta}(\rho)$  is the matrix of directional cosines, connecting coordinate system of the center-of-mass ( $\alpha = X, Y, Z$ ) with the molecule-fixed coordinate system ( $\beta = \xi, \eta, \zeta$ ), defined by the Eckart conditions<sup>5</sup> and depending on the rotational operators, and  $\mu_{\alpha} = \mu_{\alpha}(q)$  is the effective dipole moment operator, as a function of normal coordinates  $q_i$ . Following refs 26 and 94, we consider purely vibrational transitions, so that the line strength of the dipole moment transition is given by

$$S^{(ab)} = \sum_{\alpha} |\langle \Phi^{(a)} | \mu_{\alpha} | \Phi^{(b)} \rangle|^2 \quad (7.6)$$

There are two possible ways of evaluating the matrix elements in eq 7.6. According to eq 3.2, the wave functions can be obtained from the zero-order ones using explicit forms of the  $S_k$  operators

$$\Phi = U^{-1} \Phi_0 = \dots \exp(-i\lambda^2 S_2) \exp(-i\lambda S_1) \cdot \Phi_0 \quad (7.7)$$

where the exponents must be expanded in Taylor series, eq 3.4, and the terms with powers of  $\lambda$  higher than the chosen order of perturbation theory are truncated. However, there is another more convenient method of evaluation of the matrix elements in eq 7.6. Instead of transforming the zero-order wave functions, one can transform the dipole moment operator itself,<sup>26,39–45,95,96</sup> and then trivially evaluate the matrix element with the zero-order wave functions,

$$\begin{aligned} \langle \Phi^{(a)} | \mu_{\alpha} | \Phi^{(b)} \rangle &= \langle \Phi_0^{(a)} | U \mu_{\alpha} U^{-1} | \Phi_0^{(b)} \rangle \\ &= \langle \Phi_0^{(a)} | M_{\alpha} | \Phi_0^{(b)} \rangle \end{aligned} \quad (7.8)$$

In such a case, the effective operator  $\mu_{\alpha}$  expanded in a power series in normal coordinates is

$$\begin{aligned} \mu_{\alpha}(q) &= \mu_{\alpha}^0 + \sum_r \frac{\partial \mu_{\alpha}}{\partial q_r} q_r + \frac{1}{2} \sum_{rs} \frac{\partial^2 \mu_{\alpha}}{\partial q_r \partial q_s} q_r q_s \\ &+ \frac{1}{6} \sum_{rst} \frac{\partial^3 \mu_{\alpha}}{\partial q_r \partial q_s \partial q_t} q_r q_s q_t + \dots \end{aligned} \quad (7.9)$$

where the derivatives are taken at the equilibrium point. This expansion is further grouped by orders of the perturbation theory

$$\begin{aligned} \mu_{\alpha}^{[0]} &= \mu_{\alpha}^0 + \sum_r \frac{\partial \mu_{\alpha}}{\partial q_r} q_r, \quad \mu_{\alpha}^{[1]} = \frac{1}{2} \sum_{rs} \frac{\partial^2 \mu_{\alpha}}{\partial q_r \partial q_s} q_r q_s, \\ \mu_{\alpha}^{[2]} &= \frac{1}{6} \sum_{rst} \frac{\partial^3 \mu_{\alpha}}{\partial q_r \partial q_s \partial q_t} q_r q_s q_t \end{aligned} \quad (7.10)$$



At the second order, performing the double contact transformation, one obtains the following expression for the effective dipole moment operator:

$$M_{\alpha} = (\mu_{\alpha}^{[0]} + i[S_1, \mu_{\alpha}^{[0]}] - \frac{1}{2}[S_1, [S_1, \mu_{\alpha}^{[0]}]] + i[S_2, \mu_{\alpha}^{[0]}]) + (\mu_{\alpha}^{[1]} + i[S_1, \mu_{\alpha}^{[1]}]) + \mu_{\alpha}^{[2]} \quad (7.11)$$

Knowing the explicit analytical form of generators  $S_1$  and  $S_2$ ,<sup>34–36</sup> it is possible to determine the form of operator  $M_{\alpha}$  and further, according to the type of the vibrational transition (fundamental, overtone or combination), to evaluate the matrix elements in the zero-order basis.<sup>26</sup>

## 8. COMPUTER IMPLEMENTATION AND VERIFICATION OF THE ALGORITHM

The procedures and algorithms outlined above have been implemented as Fortran code, an extension of the existing package ANCO developed for the anharmonic normal coordinate analysis.<sup>83,97</sup>

Such molecular properties as electronic energy, dipole moment and polarizability can be calculated for a grid of chosen displaced configurations and then used for least-squares fitting of Taylor expansions of given power.<sup>8,98</sup> This method works well for small molecules and high-level quantum-mechanical calculations, especially when analytic first or second derivatives are not available. This procedure is less precise<sup>99</sup> than numerical differentiation, and is impractical for bigger molecules. A widely used alternative method is a numerical differentiation of available analytic derivatives of molecular properties.<sup>80,100</sup> In this work, the necessary force fields and derivatives of other molecular properties were obtained by numerical differentiation of lower-order properties (electronic energy Hessian and first derivatives of dipole moment and polarizability) calculated by means of the Gaussian03<sup>13</sup> for molecular configurations, displaced along normal coordinates using the central difference scheme.

The differentiation in one-coordinate dimension produces  $(m + n)$ th order derivatives with up to  $m+1$  different indices, where  $m$  is the order of the original molecular property and  $n$  is the order of differentiation. The two-dimensional differentiation produces  $(m + n + k)$ th order derivatives with up to  $m + 2$  different indices, where  $n, k$  are the orders of differentiation along two coordinates. The derivatives with permutations of coordinates are theoretically identical, and therefore they were averaged. Numerical differentiation in three dimensions and more is impractical except the smallest molecules.

To find out the optimum central-difference grid order and step size, we performed a series of test calculations of quadratic-to-sextic force constants for the HF (hydrogen fluoride) molecule by numerical differentiation of the electronic energy, using the MP2/aug-cc-pVTZ method, varying the step along the normal coordinate  $Q$ : 0.01, 0.015, 0.02, 0.025 Å amu<sup>1/2</sup>, and the size of the grid from three (where applicable) to 11 points. The best results were achieved for the step size 0.02 Å amu<sup>1/2</sup> (which agrees with results obtained by Császár and Mills<sup>99</sup>) and a nine-point grid. We further employed this grid for the one-dimensional differentiation up to fourth order and a  $5 \times 5$  grid for the two-dimensional numerical differentiation up to the third order along a single coordinate. These settings allowed us

to obtain up to the sextic force fields with up to four different coordinates.

The crucial point of the Fortran implementation of CVPT is the representing CAO polynomials in computer memory. For storage of a single term of the Hamiltonian  $\hat{H}$  (see eq 4.10) it is sufficient to keep a floating point coefficient and an array  $(2 \times M)$  of one byte integers of CAO powers. The number of such terms may approach hundreds of millions, and they can be stored as binary files on a hard disk and retrieved on request. The bottleneck stage of CVPT procedures is the collection of terms after the commutator evaluations and/or the summation of polynomials. We developed a two-pass algorithm which allows fast collection of terms in polynomials, the key feature of which is an encoding of CAO products as one or two 64-bit machine words. This procedure can be efficiently programmed for the MPI (message passing interface) environment on multi-processor computers.

The development of algorithms of this level of complexity and their implementation in Fortran code requires rigorous debugging and testing of results at different stages of development. We extensively used Maplesoft Maple analytic manipulation software for thorough testing of CVPT in analytic form for the one-dimensional case (diatomic molecule). Using Maple for polyatomic molecules is limited for several reasons, the main one being a very large volume of data involved in the representation of Hamiltonians. Examining the integrity of the Fortran code was performed using the following tests:

- (1) Under the condition of suppressed resonances, the transformed Hamiltonians  $\hat{H}_k^{(K)}$  for odd orders (1, 3, ...) are nil; and for even orders (2, 4, ...) only diagonal terms are present (see eq 6.16).
- (2) The second-order kinetic contribution  $T_2$  to the Hamiltonian (eq 2.2) was converted to CAO using two independent methods.
- (3) The Hamiltonian terms, rejected from the evaluation of operators  $S$  using the criterion  $|\Omega_k| < \Omega_{\text{cutoff}}$  (eq 5.2), were collected in a dedicated file, order-by-order. After completion of the CVPT procedure, the content of this file was compared with the off-diagonal terms  $\hat{H}_R$  in the fully transformed Hamiltonian and an exact match was found.
- (4) Applying the identical resonance conditions, second-order anharmonic constants  $x(r,s)$  were calculated using the analytic formulas of VPT2<sup>22</sup> and using the mixed numerical-analytic form with the aid of the new Fortran code ANCO. The resulting  $x(r,s)$  were identical to machine accuracy.
- (5) Darling–Dennison resonance coupling coefficients  $K_{rrss}$  were calculated using analytical formulas 2.8 from the literature,<sup>76</sup> and they coincided with values obtained via CVPT.
- (6) As discussed in detail below, the rule of correspondence of spectroscopic parameters  $\omega_i, x_{ij}, y_{ijk}, z_{ijkl}, \dots$  for different orders of CVPT, valid for diatomic molecules, is obeyed.

## 9. EXAMPLES, RESULTS, AND DISCUSSION

To examine the performance of our implementation of the CVPT method in higher orders, we accomplished the calculations up to the eighth order for two classic molecules: water (H<sub>2</sub>O) and formaldehyde (H<sub>2</sub>C=O) using the MP2/aug-cc-pVTZ quantum-mechanical method.

**Table 2. Harmonic and Anharmonic Frequencies for Fundamental Transitions of H<sub>2</sub>O Molecule, Obtained by the CVPT2 and CVPT4 Methods Using Three Variations of the MP2/aug-cc-pVTZ Force Field**

normal mode	harmonic (CVPT0)	$\Delta(2-0)^a$	CVPT2	$\Delta(4-2)^a$ quartic	$\Delta(4-2)$ semi-sextic <sup>b</sup>	$\Delta(4-2)$ full sextic
$\nu_1$ (A <sub>1</sub> )	3821.88	−166.54	3655.34	33.65	−5.19	0.03
$\nu_2$ (A <sub>1</sub> )	1628.37	−50.27	1578.10	−8.26	−2.60	−0.90
$\nu_3$ (B <sub>1</sub> )	3947.71	−179.78	3767.93	40.11	−8.27	2.41

<sup>a</sup>Quantities  $\Delta(2-0)$  and  $\Delta(4-2)$  denote the difference between frequencies, obtained by CVPT2 and CVPT0, and CVPT4 and CVPT2 methods, respectively. <sup>b</sup>Semi-sextic force field is obtained by one-dimensional differentiation of the Hessian producing quintic and sextic force constants of the kind  $\phi_{ijjk}$  and  $\phi_{ijkk}$ . This leads to loss of some force constants, e.g.,  $\phi_{33211} = 103.12 \text{ cm}^{-1}$  and  $\phi_{33221} = 235.69 \text{ cm}^{-1}$ .

**Table 3. Vibrational Frequencies of the H<sub>2</sub>O Molecule, Calculated at the Quantum-Mechanical Level of MP2/aug-cc-pVTZ for Different Orders of CVPT<sup>a</sup>**

normal mode	CVPT2	CVPT4	CVPT6	CVPT8	observed <sup>b</sup>
$\nu_1$ (A <sub>1</sub> )	(−166.55) 3655.34	(0.03) 3655.37	(0.89) 3656.25	(0.36) 3656.61	3657.05
$\nu_2$ (A <sub>1</sub> )	(−50.28) 1578.10	(−0.90) 1577.20	(−0.54) 1576.66	(−0.06) 1576.60	1594.75
$\nu_3$ (B <sub>1</sub> )	(−179.78) 3767.93	(2.41) 3770.34	(0.80) 3771.13	(1.84) 3772.97	3755.93

<sup>a</sup>Values in parentheses are shifts of frequencies in comparison with the previous even order of CVPT. <sup>b</sup>Observed values are taken from ref 113.

First, we have found that the sextic force field is absolutely necessary for the CVPT4 calculations. Attempts to apply a standard quartic force field, normally used for VPT2, led to unrealistic differences between fundamental frequencies obtained for CVPT4 and CVPT2 (further denoted as  $\Delta(4-2)$ ). For example, for the  $\nu_1$  mode of H<sub>2</sub>O molecule and a quartic force field,  $\Delta(4-2) = 33.65 \text{ cm}^{-1}$ , for a semisextic (see Table 2 footnote) force field,  $\Delta(4-2) = -5.19 \text{ cm}^{-1}$  and for a full sextic force field,  $\Delta(4-2) = 0.03 \text{ cm}^{-1}$ . This means that the use of a quartic force field for CVPT4 caused the error of 3 orders of magnitude! Table 2 presents a summary for all three normal modes.

The reason for this adverse result can be explained by consideration of the CVPT4 analytic form of the  $\omega_e y_e$  spectroscopic constant (Dunham constant  $Y_3^{(4)}$ ) for the one-dimensional case:

$$Y_3^{(4)} = -\frac{35}{2} \frac{\phi_3 \phi_5}{\omega} - \frac{17}{4} \frac{\phi_4^2}{\omega} + \frac{225}{4} \frac{\phi_3^2 \phi_4}{\omega^2} - \frac{705}{16} \frac{\phi_3^4}{\omega^3} + \frac{5}{2} \phi_6 \quad (9.1)$$

For the HF molecule at the MP2/aug-cc-pVTZ level of theory, accepting the zero sextic force constants  $\phi_5, \phi_6$  leads to a wrong value of  $\omega_e y_e$  ( $15.67 \text{ cm}^{-1}$ ), while using the correct values for  $\phi_5, \phi_6$  produced  $\omega_e y_e$  equal to  $0.62 \text{ cm}^{-1}$ , which is close to the observed value of  $0.93 \text{ cm}^{-1}$ .<sup>101</sup>

This consideration poses another very important question: is it legitimate to compare the CVPT2 results with ones obtained by the variational methods (VCI or VSCF), employing a quartic force field? Indeed, CVPT2 provides rather correct frequencies with a quartic force field because the derivatives originate from the Morse-type potential function. The same force field does not work with CVPT4 because it is more “sensitive” to the shape of a PES in a wider region near the equilibrium point and a quartic Taylor expansion is insufficient. The same picture is observed for the variational methods. For example, Burcl et al.<sup>102</sup> writes “the variational procedure requires that the hydrogen atoms move in regions of coordinate space beyond those in which the force field is valid”. In this connection it is necessary to recall that a Taylor expansion of a potential diverges for distances  $(r - r_e)/r_e > 1$  or  $r > 2r_e$ .<sup>103</sup>

Another important observation that follows from the inspection of Table 2 is that improvement of the sextic force field from a semisextic PES to full sextic leads to minimization of differences between frequencies obtained with CVPT2 and CVPT4. Especially impressive is such a difference for the  $\nu_1$  that equals to  $0.03 \text{ cm}^{-1}$ . This fact strongly supports the theoretical view that the slice of the PES along a symmetric stretch coordinate possesses the same feature as the Morse function, namely, the vanishing CVPT4 contribution. Even more interesting is the fact that for  $\nu_2$  (bending) the CVPT4 contribution is less than  $1 \text{ cm}^{-1}$ . This result means that either the potential energy shape for a bending deformation over a wide range can be well approximated by a Morse function or that a bending-specific function has the same property as a Morse function: vanishing fourth-order contributions.

The results of the application of CVPT6 and CVPT8 to the H<sub>2</sub>O molecule with a sextic force field (even in the light of the fact that CVPT $n$  requires  $(n+2)$ -th order PES) are presented in Table 3. Since an incorrect treatment of resonances is the main reason for divergence of the CVPT expansion, such a test must be made.

The  $\nu_1$  value predicted by the affordable QM method MP2/aug-cc-pVTZ reproduces the experimental value almost exactly, while discrepancies for  $\nu_2$  and  $\nu_3$  are of the order  $15 \text{ cm}^{-1}$  and need additional empirical correction if an exact fit is required. Such empirical corrections can be made through adjustment of harmonic frequencies,<sup>104</sup> scaling the harmonic frequencies,<sup>105,106</sup> or evaluation of the harmonic part of the force field at a higher theoretical QM level.<sup>107</sup> From Table 3 we can see that both CVPT6 and CVPT8 contributions are quite small, of the order of  $1 \text{ cm}^{-1}$ . This outcome means that substantial efforts to obtain a force field of better quality than sextic are really not worth it, especially in the light of the extreme cost of truly precise QM methods. Another observation that follows from Table 3 is that CVPT2 gives a good convergence of the whole perturbative expansion, while CVPT4 results could be considered as exact. These conclusions coincide with observations made by Pak et al.<sup>59</sup> The smallness of corrections beyond CVPT2 serves as a good proof that Dunham-type expansion 2.5 shows good convergence even for such a molecule as water, which is known to have a large-amplitude motion. Good convergence in higher orders serves as a proof that the resonances were properly accounted for.

**Table 4.** Selected Sextic Force Constants of Formaldehyde Obtained as Fourth Derivatives of the Hessian Using Two Different Quantum-Mechanical Methods (DFT–B3LYP and MP2, Using aug-cc-pVTZ Basis Sets) and Three Numerical Differentiation Grids

$\phi_{ijk}^{(6)}$	DFT–B3LYP/aug-cc-pVTZ			MP2/aug-cc-pVTZ		
	5 points grid	7 points grid	9 points grid	5 points grid	7 points grid	9 points grid
111 111	4007.07	4334.51	4349.68	1311.62	1307.39	1305.57
111 121	−62.40	−75.97	−80.62	7.66	7.72	7.71
111 122	−86.06	−87.35	−88.28	−124.84	−124.53	−124.46
111 131	−24.24	−43.09	−52.00	13.32	13.41	13.50
111 132	−167.70	−170.65	−172.56	−198.95	−198.52	−198.49
111 133	−329.88	−336.51	−340.64	−317.76	−317.17	−317.22
111 144	4274.83	4602.42	4610.88	1439.08	1437.12	1437.39
111 155	−25.30	−13.49	−4.43	−8.08	−8.40	−8.64
111 165	−345.03	−352.69	−357.43	−362.37	−361.85	−361.95
111 166	−407.35	−427.14	−439.01	−458.78	−459.15	−459.98
222 211	−8.03	−18.47	−25.44	15.19	14.98	14.90
222 221	5.37	8.74	10.91	−9.08	−9.16	−9.22
222 222	−35.52	−47.05	−53.40	38.21	38.29	38.35
222 231	3.51	8.14	11.42	−1.30	−1.32	−1.36
222 232	0.98	−0.63	−2.00	−12.96	−12.75	−12.60
222 233	−13.73	−21.36	−26.40	1.96	2.23	2.47
222 244	−6.30	−16.19	−22.77	13.34	11.02	9.57
222 255	−1.48	−5.32	−8.02	4.61	4.36	4.18
222 265	−18.12	−25.26	−30.01	−11.63	−12.60	−13.17
222 266	−5.95	−7.55	−8.60	−3.71	−3.59	−3.48

It is interesting to analyze what happens to Fermi and Darling–Dennison resonance coupling coefficients in numbers, when the order of CVPT changes from the second to the fourth. Both CVPT2 and VPT2 (see eq 2.8) for the water molecule produce same values of matrix elements (in  $\text{cm}^{-1}$ ):  $\langle 100|F_{122}^{(2)}|020\rangle = 78.26$  and  $\langle 200|F_{133}^{(2)}|002\rangle = -73.83$ , while CVPT4 yields somewhat different values:  $\langle 100|F_{122}^{(4)}|020\rangle = 69.52$ , and  $\langle 200|F_{133}^{(4)}|002\rangle = -71.57$ . As resonance coupling coefficients can be measured experimentally, it is very important to have a reliable theoretical method for their evaluation.

The performed numerical calculation allows illustrating the behavior of the general formula 6.25. For the Fermi resonance in water molecule, the coefficients in curly brackets are as follows:

(a) Second order:

$$f_0^{(2)} = 55.34, \quad f_1^{(2)} = 0, \quad f_2^{(2)} = 0, \quad f_3^{(2)} = 0$$

(b) Fourth order:

$$f_0^{(4)} = 49.15, \quad f_1^{(4)} = -2.44, \quad f_2^{(4)} = 0.39, \\ \text{and } f_3^{(4)} = -8.67.$$

The final CVPT4 effective multiresonance Hamiltonian of the  $\text{H}_2\text{O}$  molecule is a sum of expansion 6.18 plus two expansions of type 6.25, for Fermi and Darling–Dennison resonances, respectively.

Extensive calculations for bigger molecules (containing tens of atoms) require application of more economical methods and/or smaller basis sets than MP2/aug-cc-pVTZ. In a series of works (e.g., refs 80, 108, and 109), Barone and co-workers advocated the use of the hybrid density functional B3LYP (DFT), especially in combination with the 6-31+G(d,p) basis set. This QM method along with VPT2 produces an amazingly good fit to experimental frequencies for many organic

molecules, being economical at the same time. The reason for the success of the B3LYP/6-31+G(d,p) method can be attributed to mutual error cancellation effects. It was very appealing for us to use DFT with one or another basis set for our CVPT4 calculations, as this method is truly economical. However, the results were frustrating.

We made the crucial observation that the DFT–B3LYP method produced inconsistent and unreliable results beyond the quartic force field, while MP2 showed excellent stability (using aug-cc-pVTZ basis sets in both cases), as we observed for the next molecule that we tested, formaldehyde ( $\text{H}_2\text{C}=\text{O}$ ). The DFT inconsistency revealed itself as substantially different results for the sixth derivatives (i.e., fourth derivatives of analytic second derivatives) when using a different number of points for the numerical differentiation (Table 4) and lack of symmetry in numerical derivatives with permuted indices. With the DFT method, the inconsistency was up to tens of a percent, while with MP2 method, the inconsistency was 1–2 orders of magnitude smaller. Insufficient smoothness of the PES produced by the DFT method can be partially explained by the numerical integration procedure employed in Gaussian (we used options SCF=Tight, Integral=UltraFine). The averaged values of sixth derivatives at the DFT level were substantially different from results obtained at the MP2 level (Table 4).

Our major conclusion is that for the CVPT4 calculations it is compulsory to use a sextic force field and a QM method showing good consistency of results, e.g. MP2.

The fundamental frequencies, first overtones and combination bands, obtained up to the eighth order of CVPT with a four-body sextic force field for the formaldehyde molecule are presented in Table 5. First, we see that results nearly converge at fourth order, and the biggest corrections past the fourth order are  $-4.7 \text{ cm}^{-1}$  for  $2\nu_1$  and  $-3.4 \text{ cm}^{-1}$  for  $\nu_1 + \nu_5$ , while an absolute majority of other corrections are smaller than  $1 \text{ cm}^{-1}$ . Especially impressive are the small corrections for four

**Table 5. Fundamental Frequencies, First Overtones, and Combination Bands of the Formaldehyde Molecule, Calculated at Quantum-Mechanical Level MP2/aug-cc-pVTZ for Different Orders of CVPT<sup>a</sup>**

mode	CVPT2	CVPT4	CVPT6	CVPT8	Observed <sup>b</sup>
$\nu_1$ (A <sub>1</sub> )	(−139.01) 2834.36	(−3.40) 2830.97	(−0.62) 2830.35	(−0.07) 2830.28	2782.2
$\nu_2$ (A <sub>1</sub> )	(−31.80) 1721.16	(0.10) 1721.26	(0.02) 1721.28	(−0.11) 1721.17	1746.1
$\nu_3$ (A <sub>1</sub> )	(−32.34) 1507.75	(−1.01) 1506.74	(−0.05) 1506.69	(−0.14) 1506.55	1500.2
$\nu_4$ (B <sub>1</sub> )	(−16.71) 1180.17	(−1.14) 1179.04	(−0.04) 1179.00	(−0.16) 1178.84	1167.4
$\nu_5$ (B <sub>2</sub> )	(−169.86) 2877.65	(−1.62) 2876.03	(−0.35) 2875.68	(0.61) 2876.30	2843.0
$\nu_6$ (B <sub>2</sub> )	(−20.28) 1246.66	(−0.92) 1245.73	(0.02) 1245.76	(−0.16) 1245.60	1249.6
$2^*\nu_1$ (A <sub>1</sub> )	(−342.10) 5604.65	(−6.52) 5598.13	(−4.70) 5593.43	(1.16) 5594.59	5489.0 <sup>c</sup>
$2^*\nu_2$ (A <sub>1</sub> )	(−82.94) 3422.97	(−0.26) 3422.71	(0.20) 3422.91	(−0.66) 3422.25	3471.6
$2^*\nu_3$ (A <sub>1</sub> )	(−63.93) 3016.24	(−4.03) 3012.21	(−0.03) 3012.18	(−0.26) 3011.92	2998.1
$2^*\nu_4$ (A <sub>1</sub> )	(−42.06) 2351.71	(−0.60) 2351.11	(−0.09) 2351.02	(−1.18) 2349.84	2327.5
$2^*\nu_5$ (A <sub>1</sub> )	(−395.97) 5699.06	(20.67) 5719.73	(−1.59) 5718.14	(3.62) 5721.76	5651.0
$2^*\nu_6$ (A <sub>1</sub> )	(−45.38) 2488.49	(−0.28) 2488.21	(0.33) 2488.54	(−0.76) 2487.78	2496.1
$\nu_1 + \nu_2$ (A <sub>1</sub> )	(−172.38) 4553.95	(−2.04) 4551.91	(−0.73) 4551.18	(0.31) 4551.49	4529.4
$\nu_1 + \nu_3$ (A <sub>1</sub> )	(−199.31) 4314.15	(−3.09) 4311.06	(−0.85) 4310.21	(−0.13) 4310.08	4253.8
$\nu_1 + \nu_4$ (B <sub>1</sub> )	(−154.23) 4016.03	(−13.63) 4002.40	(−0.45) 4001.95	(−0.86) 4001.09	3940.2
$\nu_1 + \nu_5$ (B <sub>2</sub> )	(−387.50) 5633.39	(−16.40) 5616.99	(−3.20) 5613.79	(−1.55) 5612.24	5530.5
$\nu_1 + \nu_6$ (B <sub>2</sub> )	(−164.75) 4075.56	(−9.44) 4066.12	(−0.78) 4065.34	(−0.79) 4064.55	—
$\nu_2 + \nu_3$ (A <sub>1</sub> )	(−71.35) 3221.69	(−1.48) 3220.21	(0.01) 3220.22	(−0.50) 3219.72	3239.0
$\nu_2 + \nu_4$ (B <sub>1</sub> )	(−55.51) 2894.33	(−1.18) 2893.15	(−0.01) 2893.14	(−0.20) 2892.94	2906.0
$\nu_2 + \nu_5$ (B <sub>2</sub> )	(−234.92) 4565.55	(2.55) 4568.10	(−0.49) 4567.61	(−0.78) 4566.83	4571.5
$\nu_2 + \nu_6$ (B <sub>2</sub> )	(−26.75) 2993.14	(−7.21) 2985.93	(−0.69) 2985.24	(−0.62) 2984.62	3000.6
$\nu_3 + \nu_4$ (B <sub>1</sub> )	(−48.70) 2688.27	(−3.35) 2684.92	(−0.09) 2684.83	(−0.40) 2684.43	2667.1
$\nu_3 + \nu_5$ (B <sub>2</sub> )	(−213.14) 4374.46	(−4.02) 4370.44	(0.08) 4370.52	(1.60) 4372.12	4335.1
$\nu_3 + \nu_6$ (B <sub>2</sub> )	(−83.34) 2723.68	(5.39) 2729.07	(0.29) 2729.36	(0.60) 2729.96	2718.6
$\nu_4 + \nu_5$ (A <sub>2</sub> )	(−196.13) 4048.27	(−4.86) 4043.41	(−1.04) 4042.37	(−0.50) 4041.87	3995.8
$\nu_4 + \nu_6$ (A <sub>2</sub> )	(−29.92) 2433.90	(−2.52) 2431.38	(0.13) 2431.51	(−0.75) 2430.76	2422.4
$\nu_5 + \nu_6$ (A <sub>1</sub> )	(−205.50) 4108.95	(−7.60) 4101.35	(0.32) 4101.67	(−0.96) 4100.71	4083.1

<sup>a</sup>Values in parentheses are shifts of frequencies in comparison with the previous even order of CVPT. <sup>b</sup>Reference 111. <sup>c</sup>Reassigned value, previous assignment 5462.7 (cm<sup>−1</sup>).<sup>111</sup>

fundamental frequencies ( $\nu_2, \nu_3, \nu_4, \nu_6$ ), the differences between the fourth order and the sixth order are  $\leq 0.05$  cm<sup>−1</sup>. We conclude that convergence of the CVPT expansion is excellent, and again, the CVPT4 results should be considered as exact. There are some subtle signs of divergence at the eighth order that can be attributed to use of a sextic force field instead of the tenth-order PES.

The quality of reproduction of observed frequencies depends on the type of internal coordinate dominating the corresponding normal mode. MP2 systematically overestimates the frequencies of C–H vibrations (47.8 cm<sup>−1</sup> for  $\nu_1$ , and 33.0 cm<sup>−1</sup> for  $\nu_5$ ), which can be corrected empirically by scaling. The C–H deformations ( $\nu_3$  and  $\nu_6$ ) are reproduced very well. The CH<sub>2</sub> wagging mode ( $\nu_4$ ) demonstrates excellent convergence in fourth order, so that we can again (as for the bending mode in H<sub>2</sub>O) conclude that the potential energy function corresponding to the slice of the PES for the wagging deformation possesses the same feature as a Morse function: vanishing CVPT contributions beyond the second order.

The formaldehyde is one of the most studied four-atomic molecule and is still in the focus of attention of recent spectroscopic studies.<sup>110</sup> Advanced experimental techniques allowed precise measurements of nearly three hundred of vibrational states up to 12,500 cm<sup>−1</sup>.<sup>111</sup> Fitting experimental transitions to an empirical multiresonance Hamiltonian produced a set of experimental anharmonic constants and resonance coefficients.<sup>92</sup> These experimental constants are juxtaposed with our CVPT2 calculation in Table 6. The correspondence between the observed and predicted values is

**Table 6. Comparison of Spectroscopic Parameters  $\omega_i^0$  and  $x_{ij}$  Evaluated Theoretically by CVPT2 and Experimentally by Fitting Parameters of the Multi-Resonance Effective Hamiltonian<sup>92</sup>**

	CVPT2	observed		CVPT2	observed
$\omega_1^0$	2840.87	2809.9	$x_{33}$	−0.79	0.5
$\omega_2^0$	1730.79	1756.0	$x_{34}$	0.26	−1.2
$\omega_3^0$	1508.73	1499.4	$x_{35}$	−31.68	−21.1
$\omega_4^0$	1175.84	1167.3	$x_{36}$	2.99	−9.2
$\omega_5^0$	2910.47	2877.7	$x_{44}$	4.33	−0.9
$\omega_6^0$	1244.12	1249.8	$x_{45}$	−18.42	−20.2
$x_{11}$	−29.75	−33.8	$x_{46}$	7.07	5.5
$x_{12}$	−2.27	0.5	$x_{55}$	−34.78	−37.6
$x_{13}$	−24.16	−27.6	$x_{56}$	−29.56	−12.2
$x_{14}$	−32.75	−14.9	$x_{66}$	2.54	−0.7
$x_{15}$	−122.92	−137.0	$ k_{26,5} $	159.24	145.1
$x_{16}$	−24.79	−17.6	$ k_{36,5} $	192.88	129.3
$x_{22}$	−9.48	−9.9	$ k_{11,55} $	131.83	138.2
$x_{23}$	−8.54	−8.1	$ k_{25,35} $	25.51 <sup>a</sup>	23.2
$x_{24}$	−6.91	−7.3	$ k_{26,36} $	1.53 <sup>a</sup>	6.9
$x_{25}$	−1.93	0.9	$ k_{1,44} $	86.44 <sup>b</sup>	79.4
$x_{26}$	−6.41	−12.1	$ k_{1,66} $	61.59 <sup>b</sup>	55.0

<sup>a</sup>Matrix element given. The second-order Darling–Dennison resonance between modes 2 and 3 produces a family of matrix elements related to essentially the same (1–1) resonance. <sup>b</sup>The corresponding Fermi resonance coefficient  $W$  is four times bigger than matrix element given in the Table.

quite good, especially in the light of the large number of parameters and conceptual difference of approaches used.



Employing potential surfaces of better quality and identical forms of multiresonance effective Hamiltonians can ensure a more thorough test of the theory in the future studies.

The current article is mainly devoted to the theoretical foundations of the CVPT method and its implementation. The method is based on a systematic numerical-analytic procedure that applies up to eighth order CVPT to small polyatomic molecules (4 atoms) and fourth order CVPT (which is most important) to molecules of bigger size (we successfully treated a seven-atomic molecule). For molecules of bigger size CVPT2 remains practical. We applied it to the uracil molecule (12 atoms) without any problems, and the CPU time on a desktop computer was about 2 h.

Before the discussion of results is concluded, we would like to describe a new very important theoretical observation concerning different strategies of removal of resonances, and their effect on the interrelation of spectroscopic constants of the same kind obtained by different orders of CVPT.

Following the discussion in section 5, let us consider various possible methods of selecting resonance terms. According to the main method (A) described in section 5, the terms of Hamiltonian at any stage of the canonical transformations are assumed resonant if the quantity  $|\Omega_k|$  (eq 5.2) is greater than a certain chosen cutoff parameter  $\Omega_{\text{cutoff}}$  and the sum  $|\sum_{l=1}^M (m_{kl} - n_{kl})\omega_l|$  is smaller than certain threshold value, e.g.,  $600 \text{ cm}^{-1}$ . An alternative method (B) presumes that all resonances are known in advance and they are characterized by preset resonance patterns, which are simply products of CAO (see eq 5.1). The coefficient  $f$  in eq 5.1 is responsible for the strength of a particular resonating term in the Hamiltonian and is not a part of the pattern. In this method, the values of  $|\Omega_k|$  do not matter, the Hamiltonian terms are considered as resonant if they match one of preset patterns, identified by the user. The method (B) is convenient in applications as all resonance patterns can be found automatically and then used as preset ones, with some possible manual correction.

For comparison of methods A and B, let us recall (see eq 6.20) that in higher orders the resonance Hamiltonian terms repeat the resonance structure, but they are multiplied by increasing powers of number operators, which do not affect the value of frequency denominators in eq 5.2. The numerical coefficients of these higher orders resonance terms and consequently the quantities  $|\Omega_k|$  are generally different versus ones in lower orders and can become smaller than the  $\Omega_{\text{cutoff}}$ . Obviously, the method A does not guarantee that the resonances detected in lower orders are removed in higher orders. The method B conversely ensures that resonances are removed in all orders, in a uniform way.

For a diatomic molecule, for which the resonance effect does not occur, it can be trivially shown analytically that spectroscopic constants of the Dunham expansion 2.5 are interrelated in such a way that, for example, the constants  $\omega_e x_e$  coincide in second and fourth orders, and  $\omega_e y_e$  coincide in fourth and sixth orders, etc. Polyatomic molecules generally manifest multiple resonances, which affect the values of spectroscopic constants  $\omega_b, x_{ij}, y_{ijk}, z_{ijkl}$ , etc., so that the same type of interrelation is not necessarily the case. Our numerical calculations revealed that when the method B was employed, for all polyatomic molecules that we studied the same scheme of interrelations took place, see Table 7.

We cannot foresee all possible applications of this rule, but it obviously has a certain theoretical value. From a practical point of view, this rule could be used for the verification of results

**Table 7. Interrelation of Spectroscopic Constants of the Effective Dunham-Type Hamiltonian for Different Orders of CVPT**

constant	CVPT0	CVPT2	CVPT4	CVPT6	CVPT8
$Y(0,0)$	0	identical		identical	
$\omega(r)$	identical		identical		...
$x(r,s)$	0	identical		identical	
$y(r,s,t)$	0	0	identical		...
$z(r,s,t,u)$	0	0	0	identical	

obtained by various numerical/analytic implementations of CVPT.

## 10. CONCLUSIONS

Canonical Van Vleck perturbation theory (CVPT) is perfectly suited for anharmonic vibrational analysis of polyatomic semirigid molecules. The CVPT presents the solution in a form of a perturbative Dunham-type Hamiltonian, so that its parameters  $\omega_b, x_{ij}, y_{ijk}, z_{ijkl}, \dots$ , obtainable from quantum-mechanical potential energy surface, can be directly compared to spectroscopic constants of the effective Hamiltonians found by fitting sets of those constants to observed transitions. For diatomic molecules, CVPT provides closed form expressions for spectroscopic constants through parameters of the Hamiltonian, up to any desired order. For polyatomic molecules, an analytical solution in second order is available with a minor proviso that Fermi and Darling–Dennison ( $K_{\text{DD}}$ ) vibrational resonance coupling coefficients can be calculated in closed form, and constitute a small number of off-diagonal terms in canonically transformed quasi-diagonal Hamiltonian. This method is called second order vibrational perturbation theory (VPT2), and it is very popular and suitable for molecules of substantial size, containing dozens of atoms. Regrettably, this method may not be extended to higher orders of CVPT, because analytic expressions become practically intractable in third order. Besides, there are some other problems in VPT2 related to accurate evaluation of  $K_{\text{DD}}$  coefficients and evaluation of intensities of fundamental transitions. The higher-order CVPT $n$  are able to not only provide other spectroscopic constants, analogous to  $\omega_e y_e, \omega_e z_e, \dots$ , for diatomic molecules but also to answer some theoretical questions, such as convergence of perturbation theory in Dunham-type expansion.

An efficient approach for higher-orders of CVPT for polyatomic molecules was developed by Sibert and co-workers.<sup>11,55,59–65</sup> It is based on the representation of original and canonically transformed Hamiltonians in the form of operator polynomials, the terms of which are products of creation/annihilation operators multiplied by numerical coefficients. However, Sibert mainly employed the Meyer–Günthard–Pickett Hamiltonian,<sup>56–58</sup> suitable for curvilinear coordinates, instead of the traditional Watson Hamiltonian<sup>70</sup> written in rectilinear normal coordinates, used in VPT2. McCoy et al. showed such MGP Hamiltonian ensures better convergence of CVPT for highly excited states.<sup>62</sup>

The aim of our study was the application of the numerical–analytic technique, developed by Sibert,<sup>55</sup> to the solution of the vibrational Schrödinger equation with a Watson Hamiltonian in higher-orders of perturbation theory. This approach is more straightforward for computer implementation. In addition, it allows direct comparison with results obtained by the traditional implementation of VPT2. We have shown that

Sibert's CVPT technique works quite well for the Watson Hamiltonian.

In this article, we provided a detailed review of the necessary theoretical background and described major details necessary for software implementation of the numerical–analytic CVPT method in higher-orders. We coded the method in Fortran and tested its performance for a number of molecules. The results, obtained for the classic molecules of water and formaldehyde, are provided to demonstrate the performance of the method and to analyze the theoretical consequences.

Another major quantum mechanical method for solution of the vibrational Schrödinger equation—the variational method—requires numerical diagonalization of matrices of extraordinary size. This problem is much trickier for the numerical linear algebra methods than is the task of collecting terms in algebraic polynomials of extraordinary size that appears in CVPT for evaluation of commutators. Besides, the latter numerical task can be trivially implemented for a multiprocessor computer environment using the MPI (message passing interface), which constitutes the major trend in modern computational quantum chemistry. The current version of our software ANCO allows application of CVPT4 to molecules of about eight atoms and CVPT2 to molecules containing about 20 atoms. These limitations are comparable to those of variational techniques that currently allow calculation of vibrational energies of five-, six-, and seven-atomic molecules.<sup>16</sup>

Application of the higher-order numerical-analytic CVPT method to water and formaldehyde molecules revealed a number of important theoretical observations and rules. First of all, we have found that results obtained by VPT2 with a quartic potential may not be improved by applying more precise CVPT4 method, unless a sextic force field is introduced. This fact also means that comparison of the quartic force field VPT2 results with the variational method ones must be done with caution. A quite unexpected finding was faulty behavior of the DFT method for obtaining sextic force fields while MP2 proved its reliability. Second, we have shown that fourth-order CVPT contributions to all fundamental transitions for the water molecule that exhibit wide-amplitude motion of hydrogen atoms (the barrier to linearity is about 10,000 cm<sup>−1</sup>) are quite small and nearly nil for the symmetric stretch mode  $\nu_1$  (0.03 cm<sup>−1</sup>, see Table 3). All types of deformations, including bending, possess the similar feature as the Morse potential, for which a CVPT4 contribution vanishes. The out-of-plane symmetric wagging deformation in formaldehyde demonstrated a similar effect, which means that the underlying symmetric potential function also has vanishing fourth-order contributions, like the Morse function. The overall conclusion is that CVPT shows good convergence in second order, so that CVPT2 is proven to be a reliable method for calculation of low-lying vibrational states. For highly excited states the fourth-order spectroscopic constants  $y_{ijk}, z_{ijkl}, \dots$ , play an important role, and they can be evaluated by higher-order CVPT.

The sensitivity of the CVPT4 method to the quality of the sextic force field not only revealed the inherent problems of the DFT method but showed that the force constants comprising the sextic force field are typically interrelated in such a way that the fourth-order CVPT contribution nearly vanishes. A possible explanation is that the underlying true molecular potential for different molecules indeed possesses similar features as a Morse potential. The overall quality of a quantum mechanical force field obtained with a particular method can be examined by

comparing the theoretical fourth-order anharmonic constants  $y_{ijk}$  with experimental values.

We formulated a new scheme of removal of resonance terms, based on the dimensionless quantity  $|\Omega_k|$  (eq 5.2). The key difference with the existing scheme<sup>11</sup> is that once a resonance operator is detected, all terms of the same structure must also be removed in higher orders, even if the corresponding values  $|\Omega_k|$  are less than a control parameter  $\Omega_{cutoff}$ . Under the condition that this uniform scheme of selecting resonance terms is employed, there was an interesting theoretical finding. For all molecules that we studied, we observed that the same rule of interrelation of spectroscopic constants  $\omega_i, x_{ij}, y_{ijk}, z_{ijkl}, \dots$ , in different orders of CVPT is obeyed (Table 7), as for diatomic molecules.

In higher orders, resonance terms are multiplied by increasing powers of number operators that do not affect the physical picture of resonance itself but change the value of resonance coupling coefficient. We deduced a general formula 6.25 for expressing these coefficients. This formula may help to analyze experimental data by a reliable choice of the form of multiresonance Hamiltonians.

The straightforward procedure of obtaining the values of resonance coupling coefficients (including the most important Darling–Dennison ones) within the CVPT solution solves the theoretical problem recently posed by Matthews and Stanton: “The area of the theory in most evident need of improvement is in the calculation of the resonance strengths”.<sup>112</sup>

For a reliable interpretation of experimental spectra, it is necessary to predict the intensities of transitions of all types, which can be readily accomplished using CVPT. Availability of the explicit form of the canonical transformation operators allows transformation of the dipole moment or the polarizability tensor components and then the evaluation of IR or Raman intensities.

The final issue that is important for interpretation of spectra using CVPT is the fitting of the potential to observed transitions. In our opinion, one of the best alternatives is fitting of harmonic frequencies in such a way that anharmonic frequencies match observed values. Then, it is possible to find optimum scale factors that modify the harmonic part of the force field and ensure the best fit to optimized harmonic frequencies. Such scale factors can be further transferred to a molecule of similar structure, so that its spectrum is therefore fully “predicted”.

The method that was described in this article is well suited for theoretical analysis of anharmonic vibrations and can be used anywhere in place of traditional VPT2 as a more strict and precise alternative. For molecules of smaller size we recommend evaluating the sextic force field and applying CVPT4. For bigger molecules CVPT2 with a “semidiagonal” quartic force field will suffice.

In subsequent publications, we will describe the applications of this method to molecules of larger size and discuss in detail certain issues that were not covered here.

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### Notes

The authors declare no competing financial interest.

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