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Anharmonic Vibrational Analysis of the Gas-Phase Infrared Spectrum of 1,1-Difluoroethylene Using the Operator Van Vleck Canonical Perturbation Theory

Sergey V. Krasnoshchekov,^{*,†} Norman C. Craig,[‡] and Nikolay F. Stepanov[†]

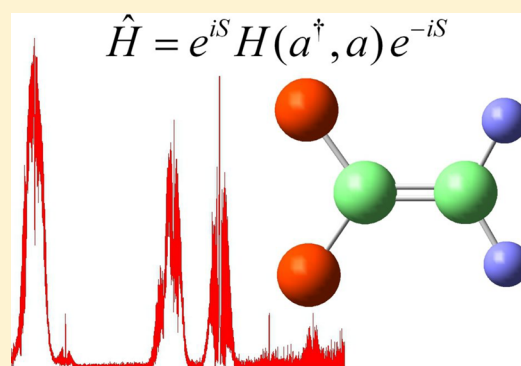
[†]Lomonosov Moscow State University, Leninskiye Gory, 119991 Moscow, Russian Federation

[‡]Department of Chemistry and Biochemistry, Oberlin College, Oberlin, Ohio 44074, United States

S Supporting Information

ABSTRACT: Anharmonic vibration frequencies of 1,1-difluoroethylene (11DFE) in the gas phase are predicted by means of the numerical-analytic operator version of the canonical van Vleck perturbation theory in the second and fourth orders (CVPT2 and CVPT4). The full quartic and “semi-diagonal” sextic rectilinear normal coordinate potential energy surfaces, needed for CVPT2 and CVPT4, respectively, were obtained with the MP2/cc-pVTZ quantum-mechanical model. CVPT2 is superior to the traditional second-order vibrational perturbation theory approach (VPT2) because of the uniform general treatment of the Fermi and second-order Darling–Dennison resonances. The fourth-order version, CVPT4, provides a more refined solution and proves convergence of the perturbative treatment. Labeling of the basis functions by polyad numbers breaks down the infinite Hamiltonian matrix into a block-diagonal form.

The polyad expression for 11DFE has been determined as $P = 14(\nu_1 + \nu_7) + 8\nu_2 + 6(\nu_3 + \nu_8) + 4(\nu_4 + \nu_9) + 3(\nu_6 + \nu_{11} + \nu_{12}) + 2(\nu_5 + \nu_{10})$, where the ν_i are quantum numbers. The theoretical prediction of anharmonic infrared absorption intensities corroborated an assignment of the majority of observed gas-phase bands up to 3500 cm^{-1} . The solution was refined by iteratively fitting harmonic frequencies, until predicted fundamental anharmonic frequencies matched the observed values. The average error for about 90 observed frequencies after fitting only fundamental frequencies is $\sim 1.05\text{ cm}^{-1}$. The fitted “semi-experimental” harmonic frequencies agree very well the quantum-mechanical predictions based on the CCSD(T)/cc-pVTZ and CCSD(T)/cc-pVQZ models.



1. INTRODUCTION

The structure and the vibration spectra of the 1,1-difluoroethylene (11DFE) molecule have recently drawn much attention.^{1–4} This six-atomic molecule is sufficiently varied to be interesting for spectroscopic studies, and at the same time, it is also small enough to be amenable to high levels of current theoretical quantum-mechanical and high-order perturbation theory methods. In the most recent work, infrared (IR) spectra of the gas phase and a liquid argon solution of 11DFE and its deuterium and ¹³C isotopologues were measured and interpreted in detail.^{1,2}

In this new work we have attempted to refine the interpretation of the experimental spectra reported in ref 1. To do so, we have used a more advanced theoretical approach than the traditional second-order vibrational perturbation theory (VPT2) employed earlier. We used a numerical-analytic operator version of the canonical van Vleck perturbation theory (CVPT) in the second and fourth orders. The difference between these similar (in theory) methods is that VPT2 is based on a set of closed expressions for anharmonic constants, resonance coefficients, etc., derived for a general case, whereas CVPT solves the Schrödinger equation every time from scratch,

with adjustments being made in response to the numerical content of the Hamiltonian. As a consequence, resonances are properly identified and treated. Besides, the CVPT approach is free of some principal limitations of VPT2; for instance, CVPT can be easily extended to higher order than second.

Second-order perturbation theory was developed in detail by Nielsen and co-workers^{5,6} in the 1950s and further refined in a number of publications. A good description of VPT2 can be found in monographs,^{7,8} reviews,^{9–12} and textbooks.¹³ Since the 1980s, several computer codes^{14–17} were written implementing VPT2 formulas, and more recently VPT2 treatment was added¹⁸ to a popular electronic structure package Gaussian03 (G03).¹⁹ Within VPT2, the parameters of the Dunham-type expansion, known as anharmonic constants x_{rs} , are expressed analytically through parameters of the Watson Hamiltonian,²⁰ such as harmonic and anharmonic force constants, rotational constants, and Coriolis coupling coefficients.⁹ In the presence of resonances, for the full

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diagonalization of the Hamiltonian it is necessary to solve an additional variational problem with a reduced basis set. For this purpose, a number of Fermi (first-order) and Darling–Dennison (second-order) off-diagonal resonance coupling coefficients are evaluated and absorbed by a numerical diagonalization. Fermi resonance constants W (two types of vibrational quantum numbers interchange: 1–2 and 1–11) can be obtained trivially as matrix elements of cubic resonance terms of the original Hamiltonian. In contrast, the Darling–Dennison constants (K_{DD})^{21–30} have seven types (1–1, 2–2, 2–11, 11–11, 1–21, 1–111, 1–3) and can be obtained as off-diagonal matrix elements of the once-transformed Hamiltonian $\tilde{H}^{(1)}$.^{21–30} Trouble with these constants arises because the analytical expression for $\tilde{H}^{(1)}$ includes first-order Fermi-resonance terms that must be removed beforehand for the correct result. This problem can be partly solved by removing terms with resonance denominators in the general analytical expressions for K_{DD} ,²⁷ but this procedure does not ensure an exact result. The troubles associated with evaluation of K_{DD} are recognized and well documented in the literature.^{27,29,31} For example, Matthews et al. write, “The area of the theory in most evident need of improvement is in the calculation of the resonance strengths”.³¹ One possible solution is solving the inverse problem, i.e., fitting Fermi and Darling–Dennison resonance constants in isolated Hamiltonian blocks to observed values of multiquanta transitions, that participate in multiple resonances. This approach was successfully used in the previous paper¹ on the 11DFE molecule and allowed an interpretation of the majority of the observed transitions. Finally, a proper implementation of VPT2 requires both a full quartic force field (not merely the “semi-diagonal” evaluation in G03¹⁹) to identify all types of Fermi and K_{DD} constants and at least a basis set including all basis functions with total quanta of excitation less than or equal to 3.

The operator version of the canonical van Vleck perturbation theory^{32–34} (CVPT) provides a more general approach to the anharmonic vibrational problem than VPT2. In 1970, Birss and Choi³⁵ pointed out the substantial simplification of CVPT if creation and annihilation operators are used instead of traditional coordinates and momenta. A detailed review can be found in the monograph by Makushkin and Tyuterev published in 1984.³⁶ These ideas were successfully developed by Sibert in the late 1980s.^{37,38} He suggested a method, suitable for a polyatomic molecule, that employed a mixed numerical-analytic representation of the Hamiltonian at all stages of canonical transformations. Finally, the transformed Hamiltonian contains primarily diagonal operators that immediately produce anharmonic constants, plus off-diagonal operators that form the corresponding families of the resonance coupling matrix elements, which are absorbed by a subsequent numerical diagonalization. However, Sibert used an alternative form of the Hamiltonian expressed by Mayer, Günthard, and Pickett (MGP) in curvilinear normal coordinates.^{39,40} Sibert’s method^{37,38} can be readily adapted to the Watson Hamiltonian.

The density of transitions for molecules of the size of 11DFE is quite high, especially in the important region of C–H stretch vibrations (about 3000 cm^{−1}). Thus, it is very useful to be able to predict not only the frequencies of transitions but also their intensities (infrared and Raman). The analytical expressions for anharmonic intensities of both fundamental (0–1) and two-quanta transitions (0–11, 0–2) are available in the literature for infrared^{41–44} and Raman spectra.^{45–47,44} However, the full picture of vibrational states can be more complicated because

other multiquanta transitions can be involved. In addition, multiquanta transitions can gain intensity from “bright” states, thereby affecting the intensities of the 0–1, 0–2, and 0–11 transitions. To describe a full picture of vibrational intensities, it is necessary to obtain the analytic expressions of transitions of other types (0–3, 0–12, 0–111, etc.) and to have anharmonic vibrational states that reflect correctly the mixing of the zero-order states. Therefore, the problem of the Fermi and Darling–Dennison resonance coupling coefficients must be solved to obtain a reliable evaluation of the intensities.

There is another less evident aspect of evaluating vibrational states of molecules bigger than three/four-atoms. For the classical, well-studied small molecules, like water, formaldehyde or acetylene, it is customary to label the vibrational states with so-called polyad quantum numbers.^{48,49} From the physical point of view, the states with the same polyad number can be strongly mixed (symmetry conditions permitting) by resonances, whereas the interpolyad-block mixing is negligible and fully “absorbed” into anharmonic constants. Availability of the polyad quantum number structure for a particular molecule, which is a set of non-negative integer coefficients corresponding to each vibrational mode, allows not only creating full basis sets for each polyad number but also identifying regions of strongly interacting states. The former advantage means that the infinite Hamiltonian matrix decomposes into block-diagonal form, each block having a finite manageable size (provided all polyad coefficients are nonzero). Therefore, an exact variational solution can be obtained. Although the polyad technique had proven its efficiency, there are very few examples of using it on molecules bigger than four-atoms. Evaluation of the polyads for small molecules is straightforward,^{49,50} but for the bigger molecules no general method is recognized. So far, the polyad method has not been used for vibrational analyses of any fluoro-substituted ethylenes. Two of us (S.V.K. and N.F.S.) have developed a new efficient method of evaluation of polyad coefficients⁵¹ that is here employed for 11DFE. The major features of using polyad numbers are described in the Theoretical Section.

In this work we employ the perturbation theory method that uses harmonic frequencies (ω_r) as zero-order parameters, which in turn affect both the anharmonic constants and the resonance coupling constants. By fitting the values of ω_r so that the final anharmonic frequencies of fundamentals match the observed vibrational band centers, one can obtain “experimental” values of *harmonic* frequencies that can be directly compared to a higher-level quantum mechanical counterpart.

This work had two main goals. The primary goal was obtaining a more reliable theoretical prediction of the IR spectra of 11DFE with minimum involvement of an experimentalist and a minimum of adjustable parameters. The previous work¹ is here enhanced by evaluation of IR intensities and use of the polyad technique. We tested the accuracy and ease of use of the CVPT method that ideally works in a “black-box” manner. The second goal was to take a step forward in finding a methodology for predicting vibrational spectra without any involvement of empirical knowledge drawn from the spectrum of a molecule.

2. THEORY

In this section we briefly describe the main theoretical points important for understanding the method applied for the modeling of the vibrational spectra of 11DFE: the choice and form of the Hamiltonian, main features and deficiencies of the

traditional second-order vibrational perturbation theory (VPT2), the machinery of the operator version of the canonical van Vleck perturbation theory (CVPT), the variational step and construction of the polyad quantum number (PQN), and evaluation of the infrared intensities. More details can be found in the recent publication by two of us (S.V.K. and N.F.S.).⁵²

2.1. Hamiltonian. For the anharmonic vibrational analysis of a polyatomic molecule, it is customary⁹ to expand the Watson Hamiltonian $H = T + V$ in powers of rectilinear dimensionless normal coordinates $q_r = Q_r[4\pi^2c^2\omega_r(hc)^{-1}]^{1/2}$, where ω_r is a harmonic frequency and Q_r is Wilson's normal coordinate.⁵³ The potential energy operator V expansion is usually limited to the quartic force field,

$$\begin{aligned} V &= V_0 + V_1 + V_2 \\ &= \frac{1}{2} \sum_r \omega_r q_r^2 + \frac{1}{6} \sum_r \sum_s \sum_t \phi_{rst} q_r q_s q_t \\ &\quad + \frac{1}{24} \sum_r \sum_s \sum_t \sum_u \phi_{rstu} q_r q_s q_t q_u \end{aligned} \quad (1.1)$$

but needs to be extended up to the fourth-order terms (sixth force field) for the corresponding order of perturbation theory. The kinetic energy operator²⁰ is a sum of the zero-order terms, expressed through the conjugate momenta $p_r = -i(\partial/\partial q_r)$, and the second-order terms of the Coriolis coupling operators $\hat{\pi}_\alpha$ at the zero eigenvalue of the rotational operator ($J = 0$),

$$\begin{aligned} T &= T_0 + T_2 = \frac{1}{2} \sum_r \omega_r p_r^2 + \sum_{\alpha=x,y,z} B_e^\alpha \pi_\alpha^2 \\ \pi_\alpha &= \sum_r \sum_s \zeta_{rs}^\alpha \left(\frac{\omega_s}{\omega_r} \right)^{1/2} q_r p_s \end{aligned} \quad (1.2)$$

Here equilibrium rotational constants are designated as B_e^α and Coriolis coupling constants are designated as ζ_{rs}^α . The summations in eq 1.1 and eq 1.2 are performed over all of vibrational degrees of freedom, M . To simplify the formalism, we shall only deal with nondegenerate modes. The Hamiltonian $H = T + V$ grouped by orders of perturbation theory is given by

$$\begin{aligned} H &= T + V = \left[\frac{1}{2} \sum_r \omega_r (p_r^2 + q_r^2) \right] + \left[\frac{1}{6} \sum_r \sum_s \sum_t \phi_{rst} q_r q_s q_t \right] \\ &\quad + \left[\frac{1}{24} \sum_r \sum_s \sum_t \sum_u \phi_{rstu} q_r q_s q_t q_u \right] \\ &\quad + \sum_{\alpha=x,y,z} B_e^\alpha \left(\sum_r \sum_s \sum_t \sum_u \zeta_{rs}^\alpha \zeta_{tu}^\alpha \left(\frac{\omega_s}{\omega_r} \right)^{1/2} \left(\frac{\omega_u}{\omega_t} \right)^{1/2} q_r p_s q_t p_u \right) \end{aligned} \quad (1.3)$$

where ϕ_{rstu} etc. are force constants (in cm^{-1} units) expressed in dimensionless normal coordinates.

We have chosen the Watson Hamiltonian for a number of reasons, mainly to give direct correspondence between our CVPT study and traditional VPT2 and to fulfill the aim of applying our method to bigger molecules. For example, re-expressing the Watson Hamiltonian in creation and annihilation operators (CAO) is a straightforward analytic procedure, whereas the MGP-Hamiltonian required high-order numerical differentiation and produced more terms.

2.2. Second-Order Vibrational Perturbation Theory (VPT2) and Resonances. Applying Rayleigh–Schrödinger or canonical van Vleck perturbation theory in second order,^{5–11} one obtains the analytic expressions for anharmonic constants x_{rs} for a Dunham-type expansion,

$$E(hc)^{-1} = E_0 + \sum_r^M \omega_r \left(v_r + \frac{1}{2} \right) + \sum_{r \leq s}^M x_{rs} \left(v_r + \frac{1}{2} \right) \left(v_s + \frac{1}{2} \right) \quad (2.1)$$

and expressions for Fermi $W_{r,ss}$, $W_{r,st}$, and Darling–Dennison resonance coupling off-diagonal constants $K_{rr,ss}$, The expressions for both anharmonic and resonance constants are widely available in the literature,^{8–11,54,55} and it is not necessary to reproduce them here.

As stated in the Introduction, the published expressions for second-order Darling–Dennison resonance constants are derived on the assumption that there are no first-order resonances. This simplification is of course not the case. The resonance terms can be removed from the expressions for Darling–Dennison constants “manually”,²⁷ but this procedure is not an algebraically strict one.⁵⁶ It should be noted that using the full quartic force field is necessary for evaluation of all types of Darling–Dennison constants as the constant $K_{r,stu}$ requires values of force constants ϕ_{rstu} .

2.3. Canonical Van Vleck Perturbation Theory (CVPT). The canonical Van Vleck perturbation theory (CVPT)^{32–36} involves working with the operator representation of both the original Hamiltonian (e.g., in the Watson form eq 1.3) and all its transformed intermediate forms, order-by-order of perturbation theory. A full explanation of the machinery of the CVPT can be found elsewhere, but it is worthwhile reminding the reader of its basic ideas, as it is important for understanding of the subsequent material.

First, the goal is to re-express the original Hamiltonian in an equivalent form, for which the eigenvalues remain intact. The transformation that does this job must meet two requirements: it obviously does not change eigenvalues, and it is chosen in such a form that eigenfunctions of the transformed Hamiltonian are known beforehand. The role of such eigenfunctions is played by the products of harmonic oscillator wave functions, for which it is trivial to write out matrix elements. The transformation of the type needed is chosen in the following exponential form:

$$\begin{aligned} \hat{H} &= U H U^{-1} & U &= \exp(iS) & U^{-1} &= \exp(-iS) \\ U^{-1} U &= I \end{aligned} \quad (3.1)$$

where S is a Hermitian operator and U is a unitary one. There are several ways to find S operators. They can be simply chosen in a suitable form, as was done in the early days of the development of this theory.^{5–7} Alternatively, they can be found by solving systems of linear equations.^{57,58,8} To make the whole problem tractable (to avoid summation of an infinite series of operators), powers of the perturbation parameter λ are introduced both into the Hamiltonian expansion and into the unitary operator, $U = \exp(i\lambda S)$. Afterward, it becomes possible to represent a solution as a sum of contributions of increasing orders, because the equations are broken down by powers of λ .

In 1970, Birss and Choi³⁵ suggested that the whole scheme of canonical transformations is substantially simplified if coordinate-momentum operators are replaced by their linear combinations known as creation and annihilation operators (CAOs),

$$a^\dagger = \frac{1}{\sqrt{2}}(q - ip) \quad a = \frac{1}{\sqrt{2}}(q + ip) \quad (3.2)$$

The main useful property of CAOs is that they increase or decrease vibrational quantum numbers of the zero-order (harmonic) vibrational wave functions,

$$a^\dagger |v\rangle = \sqrt{v+1} |v+1\rangle \quad a |v\rangle = \sqrt{v} |v-1\rangle$$

$$a^\dagger a |v\rangle = \hat{N} |v\rangle = v |v\rangle \quad (3.3)$$

It can be trivially shown that once the Hamiltonian is expressed by means of CAOs using so-called normal ordering of CAOs,³⁶

$$\hat{H} = \sum_j h_j \prod_{l=1}^M (a_l^\dagger)^{m_{jl}} (a_l)^{n_{jl}} \quad (3.4)$$

and the diagonal terms with equal powers ($m_{jl} = n_{jl}$) are removed from eq 3.4, the S operators that are needed for cancellation of the off-diagonal terms in eq 3.4 are derived using the formula,^{35,36}

$$S = -i \sum_j h_j \left(\sum_{l=1}^M (m_{jl} - n_{jl}) \omega_l \right)^{-1} \prod_{l=1}^M (a_l^\dagger)^{m_{jl}} (a_l)^{n_{jl}} \quad (3.5)$$

To obtain the desired form of the transformed Hamiltonian, given by a sum of increasing order terms,

$$\hat{H}^{(K)} = H_0 + \sum_{k=1}^K \hat{H}_k^{(K)} \quad (3.6)$$

one needs to evaluate each of these terms in eq 3.6 using the following general expression,^{59,60,46}

$$\hat{H}_k^{(K)} = \hat{H}_k^{(K-1)} + \sum_{m=0}^{l-1} \frac{i^{l-m}}{(l-m)!} \underbrace{[S_K, [S_K, \dots [S_K, \hat{H}_{K+m+L}^{(K-1)}] \dots]]}_{l-m} \quad (3.7)$$

where $l = (k - L)/K$ and $L = \text{mod}(k, K)$ is the remainder of the division of k by K . Evaluation of the commutators in eq 3.7 can be done in a straightforward manner using the formula:^{37,47}

$$(a^\dagger)^k a^l (a^\dagger)^m (a)^n = (a^\dagger)^{k+m} (a)^{l+n}$$

$$+ \sum_{i=1}^{\min(l,m)} \left[\frac{1}{i!} \prod_{j=0}^{i-1} (l-j)(m-j) \right] (a^\dagger)^{k+m-i} (a)^{l+n-i} \quad (3.8)$$

Resonance terms in the Hamiltonian (eq 3.4) can be recognized^{52,61} by abnormal values of the dimensionless quantity Ω_k ,

$$|\Omega_k| = \left| h_k \left(\sum_{l=1}^M (m_{kl} - n_{kl}) \omega_l \right)^{-1} \right| > \text{TolSop} \quad (3.9)$$

or merely by small values of the denominator in eq 3.9, lying under the threshold value “TolDen”, typical values of which are 200–300 cm⁻¹. As pointed out by Martin et al.,⁶¹ it is the ratio of the Hamiltonian coefficient and the denominator in eq 3.9 that matters, rather than the denominator itself. Attempting to ignore resonance operators in eq 3.4 leads to values of anharmonic constants that are too big and thus cause a breakdown in the perturbative expansion. Typically,⁵² the threshold value “TolSop” of the quantity Ω_k lies in the region 0.01–0.10. If the value of Ω_k related to a term in eq 3.4 is smaller than “TolSop”, then the corresponding S -operator term is created, and therefore, the interaction is accounted for

perturbatively. Otherwise, terms with $\Omega_k \geq \text{TolSop}$ do not participate in preparation of the S operators (eq 3.5). They are retained in the transformed Hamiltonian and treated further variationally.

2.4. Polyad Quantum Number. Due to the presence of resonance effects, the solution of the vibrational Schrödinger equation requires not only the evaluation of anharmonic coefficients, x_{ijp} , y_{ijk} , z_{ijkl} , ..., that constitute the Dunham-type expansion (eq 2.1) but also the solution of an additional variational problem for the remaining off-diagonal resonance operators to reduce the Hamiltonian into a diagonal matrix form.

As the Hamiltonian has a quasi-diagonal form after applying the proper canonical transformations, in the framework of traditional VPT2 calculations, the basis set can be chosen in such a way that the total quanta of vibrational excitation in basis functions are limited to 2, 3, or 4. This condition means that some connected states are not considered.

If an accurate solution or an analysis of how the truncation of the basis set affects the final solution is required, it is generally not satisfactory to limit the basis set at low levels of vibrational excitation. Instead, the basis set must be increased until the “variational limit” is achieved. This elaboration creates a great difficulty as the necessary basis sets are really huge. Dealing with such problems requires extraordinary computer and time resources. For example, for a 10-atomic molecule, a basis set with maximum excitation equal to 4 is greater than 20 000 basis functions.

Although this problem seems to be a stumbling stone, there is an elegant solution that avoids big basis sets and yields “exact” solutions (in a certain sense) with basis sets of much smaller size. Of course, such a situation occurs if the infinite Hamiltonian matrix is decomposed to a block-diagonal form, for which it is necessary to apply some additional conditions. It is well-known from vibrational analyses of small molecules, such as water,⁶² acetylene,⁶³ formaldehyde,⁶⁴ and phosphacetylene⁶⁵ (HCP) that each vibrational state can be labeled by a polyad quantum number (PQN). To calculate the values of PQN (designated P), it is necessary to know the values of non-negative integer weight coefficients p_i assigned to each vibrational mode, that are used in summation of individual quantum numbers v_i over all modes. For example, for the formaldehyde molecule, the polyad expression is as follows:

$$P = \sum_{i=1}^M p_i v_i = 2(v_1 + v_5) + v_2 + v_3 + v_4 + v_6 \quad (4.1)$$

The values of integer coefficients p_i are approximately proportional to “contributions” of excitations of individual normal modes to the total vibrational energy of the molecule. If all polyad coefficients are nonzero, the Hamiltonian can be approximated by a block-diagonal form, so that within each block of finite-size all vibrational states (basis functions) have the same value of PQN. The sizes of blocks are typically manageable, from a few to a few hundred states. It is not necessary to diagonalize all blocks, because the spectral range of interest is usually limited.

The term “polyad” is normally used to mean a group of vibrational states interconnected through resonances. The polyad blocks introduced through the definition of the eq 4.1 kind can unite vibrational states (and basis functions) of more than one symmetry type and therefore consist of sub-blocks,

which simplify the classification of states and the diagonalization process.

The question arises of how to find the values of the coefficients of the polyad expression.^{49–51} The vector of polyad coefficients must be orthogonal to all vectors composed of powers of individual CAOs belonging to resonance operators (the powers of creation operators produce positive coefficients and annihilation operators negative coefficients).^{49–51} Kellmann's polyad vector method⁴⁹ states that the dimension of polyad vector space is the difference between the whole vibrational space ($M = 3N_{\text{atom}} - 6$, for a nonlinear molecule) and the dimension of resonance vector space.

There is some flexibility in choosing the set of resonance operators, as smaller resonance interactions can be alternatively accounted for by “absorbing” them into anharmonicity coefficients or treating them variationally as off-diagonal elements of the Hamiltonian. Accordingly, the form of a polyad vector will be ambiguous. For the “best” PQNs all coefficients are positive, and they must ensure an optimum block-diagonal structure. The bigger the molecule is, the more complicated the procedure of finding PQN becomes.⁵¹ The right strategy is to “admit” the $M - 1$ strongest linearly independent resonances and their linear combinations, whereas all the remaining resonance must be “absorbed” into anharmonic constants perturbatively.^{50,51} We would like to stress that CVPT is well suited to finding the PQNs. The form of PQN for the 11DFE and the method of its evaluation is described below in section 3.

2.5. Infrared Intensities. When an explicit form of the canonical transformations (given by S operators) is known, it is convenient to evaluate matrix elements of an arbitrary physical quantity operator Ξ using the following rearrangement:

$$\begin{aligned}\langle \Phi^{(a)} | \Xi | \Phi^{(b)} \rangle &= \langle (U^{-1} \Phi_0^{(a)}) | \Xi | U^{-1} \Phi_0^{(b)} \rangle \\ &= \langle \Phi_0^{(a)} | U \Xi U^{-1} | \Phi_0^{(b)} \rangle\end{aligned}\quad (5.1)$$

In other words, instead of taking matrix elements in anharmonic functions, the canonical transformation is applied to a polynomial expansion of the operator Ξ itself and matrix elements are taken trivially with harmonic wave functions $\Phi_0^{(a)}$, $\Phi_0^{(b)}$. This approach can be conveniently applied to finding infrared intensities, which are functions of transition dipole moments. For the Boltzmann distribution of molecules at absolute temperature T the integral absorption coefficient of electric dipole moment $a \leftarrow b$ is given by the following formula:^{66,67}

$$I^{(ab)} = \int \epsilon(\nu) d\nu = \frac{8\pi^3 N_A}{3hcQ} \nu^{(ab)} S^{(ab)} [e^{-E^{(b)}/kT} - e^{-E^{(a)}/kT}] \quad (5.2)$$

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

$$S^{(ab)} = \sum_{\alpha} |\langle \Psi^{(a)} | M_{\alpha} | \Psi^{(b)} \rangle|^2 \quad (5.3)$$

where $\Psi^{(a)}$ and $\Psi^{(b)}$ are full wave functions, corresponding to the nondegenerate eigenstates $E^{(a)}$ and $E^{(b)}$, and M_{α} is the α component of the molecular dipole moment operator in the space-fixed coordinate system ($\alpha = X, Y, Z$). 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 with eq 5.3. In this case eq 5.3 is reduced to

$$S^{(ab)} = \sum_{\alpha} \left| \langle \Phi^{(a)} | \sum_{\beta} \varphi_{\alpha\beta} \mu_{\alpha}(q) | \Phi^{(b)} \rangle \right|^2 \quad (5.4)$$

where the $\Phi^{(i)}$ are the vibration–rotation wave functions, $\varphi_{\alpha\beta}(\rho)$ is the matrix of directional cosines, connecting the 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 conditions⁶⁶ and depending on the rotational operators. Here $\mu_{\alpha} = \mu_{\alpha}(q)$ is the effective dipole moment operator, depending on the normal coordinates q_i . Following refs 41 and 68, we consider purely vibrational transitions, so that the line strength of the dipole moment transition is given by

$$S^{(ab)} = \sum_{\alpha} |\langle \Phi^{(a)} | \mu_{\alpha} | \Phi^{(b)} \rangle|^2 \quad (5.5)$$

Such matrix elements can be found^{41,68–76} in the manner outlined in the beginning of the section,

$$\langle \Phi^{(a)} | \mu_{\alpha} | \Phi^{(b)} \rangle = \langle \Phi_0^{(a)} | U \mu_{\alpha} U^{-1} | \Phi_0^{(b)} \rangle = \langle \Phi_0^{(a)} | M_{\alpha} | \Phi_0^{(b)} \rangle \quad (5.6)$$

once the effective operator μ_{α} is expanded in a power series and the terms are grouped by orders,

$$\begin{aligned}\mu_{\alpha}(q) &= \left[\mu_{\alpha}^0 + \sum_r \left(\frac{\partial \mu_{\alpha}}{\partial q_r} \right)_0 q_r \right] + \left[\frac{1}{2} \sum_{rs} \left(\frac{\partial^2 \mu_{\alpha}}{\partial q_r \partial q_s} \right)_0 q_r q_s \right] \\ &+ \left[\frac{1}{6} \sum_{rst} \left(\frac{\partial^3 \mu_{\alpha}}{\partial q_r \partial q_s \partial q_t} \right)_0 q_r q_s q_t \right] + \dots\end{aligned}\quad (5.7)$$

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

$$\begin{aligned}M_{\alpha} &= \left(\mu_{\alpha}^{[0]} + i[S_1, \mu_{\alpha}^{[0]}] - \frac{1}{2}[S_1, [S_1, \mu_{\alpha}^{[0]}]] + i[S_2, \mu_{\alpha}^{[0]}] \right) \\ &+ (\mu_{\alpha}^{[1]} + i[S_1, \mu_{\alpha}^{[1]}]) + \mu_{\alpha}^{[2]}\end{aligned}\quad (5.8)$$

2.6. Fitting Procedures. One of the popular methods of adjusting the calculated harmonic frequencies is scaling of the quadratic force field.^{77–81} In this method, various contributions to the differences between calculated harmonic and observed frequencies are “absorbed” into scale factors that adjust both diagonal force constants directly and off-diagonal force constants by the geometric mean of the corresponding multipliers for diagonal force constants. This type of adjustment of the force field possesses a substantial phenomenological character, partly because fundamental frequencies can be affected by resonance shifts of unpredictable direction and sign. However, for bigger-sized molecules this method remains the only one available, as both the variational and perturbative methods require higher-order potential surfaces and can be inapplicable for floppy molecules.

In the case of an anharmonic calculation by perturbation theory, the harmonic force field can be nicely scaled to fit the fundamentals to observed values, but a question arises about what to do with the anharmonic part. We believe that the cubic

and higher-order anharmonic force constants should remain unaffected during the scaling procedure for two reasons. First, as explained by Allen and Császár,⁸² the quality of quantum-mechanical prediction of anharmonic force field is often higher than for the quadratic part. Second, cubic and higher-order force field contributions to anharmonic constants are much smaller than from quadratic contributions. Overall, as will be shown below, adjustment of only the quadratic force field is sufficient for achieving adequate results in case of the 11DFE molecule.

An elegant way to fit the calculated fundamental frequencies to observed values was proposed by Miani et al.⁸³ for the anharmonic analysis of benzene. In this procedure, the harmonic frequencies are iteratively adjusted by the differences between observed and calculated fundamental frequencies. Sometimes the functional dependence of fundamentals from harmonic frequencies can be discontinuous, which prevents convergence to exact values, but generally this technique works well.

The outstanding question now is how to transfer the adjustments of the frequencies to adjustments of the harmonic force field and to find the values of scale factors, which would effectively correct the original field. The scale factors can be useful for predicting the vibrational spectrum of the molecules of similar structure. The obvious solution is to “convert” values of adjusted harmonic frequencies back into harmonic force constants and then find the values of scale factors by comparing diagonal force constants with the original ones. This conversion can be accomplished in straightforward manner by the following equality, known from Wilson’s GF matrix method,⁵³

$$F_R = L^{-1} \Lambda (L^{-1})^T \quad (6.1)$$

If squared frequency terms Λ are replaced by “observed” squared frequency terms $\Lambda^{(\text{obs})}$, the resulting force constant matrix $F_R^{(\text{obs})}$ would reproduce them in a secular equation,

$$GF_R^{(\text{obs})}L = \Lambda^{(\text{obs})}L \quad (6.2)$$

The desired scale factors can be obtained as the diagonal values of the “experimental” $F_R^{(\text{obs})}$ divided by the ones of the raw quantum-mechanical counterpart, $F_R^{(\text{QM})}$:⁸⁴

$$s_i = (F_R^{(\text{obs})})_{ii} [(F_R^{(\text{QM})})_{ii}]^{-1} \quad (6.3)$$

3. CALCULATION DETAILS

The geometry optimizations of the 11DFE molecule and calculations of the Hessian (quadratic force constants) at equilibrium and for all displaced configurations (see details below) were accomplished by means of the G03 program package.¹⁹ The main calculation of the optimized geometry and sextic force field was made exclusively by the second-order Møller–Plesset electronic perturbation theory (MP2) using the Dunning correlation consistent basis set (cc-pVTZ). The “VeryTight” geometry optimization criterion¹⁹ and “NoSymm” (ignoring simplifications due to molecular symmetry) options were applied. The reason for avoiding the utilization of molecular symmetry by G03 was instability of results of numerical differentiation of the Hessian at displaced configurations when the symmetry changed at different points of the grid.

All anharmonic vibrational computations, except the electronic structure ones, were performed with the aid of our software package ANCO (acronym for Analysis of Normal

Coordinates),⁵² designed for anharmonic vibrational normal coordinate calculations. This software is written in Fortran and available for Windows and Linux operating systems. The electronic structure calculations were performed at Oberlin College or at the Ohio Supercomputer Center (OSC). The calculations with the CCSD(T) models were done with Gaussian09 (G09) at the OSC. The interaction of ANCO with the G03 package was arranged through automated generation of G03 input files by ANCO and subsequent import of data from the G03 checkpoint files, converted into text format, once the electronic calculations for all displaced configurations were accomplished. The full quartic and “semi-diagonal” (up to four different modes) sextic potential energy surfaces were obtained by the one- and two-dimensional numerical differentiation of Hessians in normal coordinates, using the 9 and 5 × 5 equidistant grids, accordingly, and a 0.02 Å × (amu)^{1/2} step size. We have previously found⁵² that the hybrid density functional B3LYP in the G03 implementation is not quite suitable for calculation of the sextic force field, possibly due to numerical integration round-off errors, even for the “Ultrafine” grid for numerical integration. In contrast, MP2 had proven to have good stability for the evaluation of the third and fourth numerical derivatives of analytic second derivatives of the electronic energy.⁵² Calculation of the cubic surfaces of the dipole moment components was performed by the single and double differentiation of the analytic dipole moments.

The key point of the anharmonic vibrational analysis is the choice of the values of integer coefficients defining the polyad quantum number given the values of normal mode quantum numbers. As explained above in the theoretical section, the polyad form is not unique. In “good” cases the choice of the polyad vector is straightforward, once the set of resonance vectors is defined using simple selection criteria. Fortunately, the 11DFE molecule is a “good” molecule in this sense, and the necessary set of resonance vectors was obtained by a small variation of two main criteria (“TolDen” and “TolSop”) defining the resonances. Namely, the choice of “TolDen” = 300 cm^{−1} and “TolSop” = 0.08 leads to the following form of the polyad quantum number definition:

$$P = 14(\nu_1 + \nu_7) + 8\nu_2 + 6(\nu_3 + \nu_8) + 4(\nu_4 + \nu_9) + 3(\nu_6 + \nu_{11} + \nu_{12}) + 2(\nu_5 + \nu_{10})$$

where the ν_i are quantum numbers. It is worthwhile to note that all A_2 and B_2 normal modes are assembled together with the only odd coefficient, whereas all A_1 and B_1 normal modes have even ones.

There is another form of the definition, evaluated by using a more sophisticated strategy of selecting the resonance vectors:⁵¹

$$P = 4(\nu_1 + \nu_7) + 2(\nu_2 + \nu_3 + \nu_4 + \nu_5 + \nu_8 + \nu_9) + (\nu_6 + \nu_{11} + \nu_{12})$$

We did not use the latter form for the reason that one coefficient (ν_{10}) is zero, which leads to infinite blocks. All subsequent calculations were performed with a constraint that only those resonance vectors are allowed that are orthogonal to the polyad vector.

4. RESULTS AND DISCUSSION

The results of geometry optimizations by four quantum-mechanical method/basis set combinations are presented in

Table 1. Experimental and Theoretical Quantum Mechanical Geometrical Parameters (Ångstroms, Degrees) of the 1,1-Difluoroethylene Molecule

parameter, r_e	observed, r_e semiexp ^a	best composite theory ^a	MP2/cc-pVTZ	CCSD(T)/cc-pVTZ	CCSD(T)/aug-cc-pVTZ	CCSD(T)/cc-pVQZ
$r_e(\text{C}=\text{C})$	1.3175(4)	1.3181	1.3213	1.3244	1.3244	1.3214
$r_e(\text{C}-\text{F})$	1.3157(2)	1.3157	1.3171	1.3189	1.3217	1.3173
$r_e(\text{C}-\text{H})$	1.0754(1)	1.0750	1.0744	1.0772	1.0779	1.0766
$\angle(\text{C}=\text{C}-\text{F})$	125.16(2)	125.14	125.0731	125.0631	125.1856	125.1215
$\angle(\text{C}=\text{C}-\text{H})$	119.40(1)	119.39	119.2578	119.4521	119.3807	119.4046

^aReference 3.

Table 1. It is important that the reference geometry be close to the experimental one as it strongly affects the harmonic part of the potential.⁸² In our study, the agreement between the MP2/cc-pVTZ reference geometry and the experimental r_e -structure is quite good. From Table 1 it is seen that the lengths of C=C and C-F bonds at MP2/cc-pVTZ and CCSD(T)/cc-pVQZ levels are nearly equal, which is probably a consequence of error cancellations for the MP2/cc-pVTZ model.

For the correct accounting of resonances and the best possible solution of the variational problem, we employed the polyad technique, which reduces the Hamiltonian before the final diagonalization to a block diagonal form. The diagonalization of these blocks leads to the “exact” variational solution for the vibrational states constituting each block. Table 2 shows the

Table 2. Structure of Polyad Blocks ($P = 2-20$) of the Hamiltonian Matrix: Block Sizes, Frequency Ranges and Block Spans (cm^{-1}), and Symmetry Types

polyad no.	block size ^a	lower limit	upper limit	block span	symmetry
2	2	437.1	549.7	112.6	A_1, B_1
3	3	609.5	802.1	192.6	A_2, B_2
4	5	876.4	1099.4	222.9	A_1, B_1
5	6	1047.1	1352.8	305.7	A_2, B_2
6	16	1219.3	1649.0	429.7	A_1, B_1
7	15	1486.9	1903.4	416.5	A_2, B_2
8	31	1657.3	2198.6	541.3	A_1, B_1
9	40	1829.4	2454.0	624.7	A_2, B_2
10	62	2097.7	2748.0	650.3	A_1, B_1
11	77	2267.9	3004.5	736.7	A_2, B_2
12	129	2439.8	3297.2	857.5	A_1, B_1
13	146	2708.8	3554.9	846.2	A_2, B_2
14	230	2878.7	3846.2	967.6	A_1, B_1
15	283	3050.4	4105.1	1054.7	A_2, B_2
16	400	3320.1	4395.0	1074.9	A_1, B_1
17	490	3489.8	4655.1	1165.3	A_2, B_2
18	702	3661.4	4943.5	1282.2	A_1, B_1
19	824	3931.8	5204.9	1273.1	A_2, B_2
20	1152	4101.3	5491.7	1390.5	A_1, B_1

^aThe comprehensive number of basis functions corresponding to a given polyad quantum number.

number of basis functions and frequency ranges for the polyad number up to 20, after diagonalization. Frequencies were calculated using CVPT4, after fitting the predicted fundamentals to observables, as explained above in section 2.6. To cover the frequency range up to about 3500 cm^{-1} , it is sufficient to consider the polyad numbers from 2 to 16. The maximum number of basis functions in the blocks considered is equal to 400.

As it is seen from Table 2, inside each polyad there can be different symmetry types of basis functions. Consequently, the

block breaks down into sub-blocks, corresponding to different symmetries. This consideration further reduces the dimensions of the matrices to be diagonalized. The spectroscopic selection rules for different polyad and symmetry blocks can be different. Thus, a polyad number label automatically means applying certain selection rules. In the case of 11DFE, all even polyad numbers belong to A_1, B_1 symmetry types, and all odd numbers belong to A_2, B_2 . The frequency ranges of different polyad blocks overlap from about 1000 cm^{-1} up, even some of the same symmetry types. It means that frequencies in the overlapping areas, belonging to different polyads, do not have mutual resonance shifts, even if they are close to each other. The frequency range for a polyad can be quite wide; for example, for polyad number 16 the range is over 1000 cm^{-1} .

As was stressed in the section 2, the results of an anharmonic calculation are mainly affected by the accuracy of the harmonic frequencies. A good strategy is therefore to optimize the harmonic frequencies to fit the observed values of fundamentals⁸³ or, alternatively, to substitute values of harmonic frequencies obtained by a higher-level quantum-mechanical method.^{85–88} Because the MP2/cc-pVTZ quantum-mechanical model does not ensure satisfactory agreement of fundamental frequencies with experimental values (Table 5), both schemes can be used for improving the fit of fundamental frequencies on the assumption that the accuracy in reproducing overtones and combination bands will be good enough to make confident assignments of experimental bands.

We fitted the harmonic frequencies, iteratively correcting their values by the differences between predicted and observed fundamentals, until an agreement was achieved. For predicting the fundamental frequencies of molecules of similar structure or 11DFE isotopologues, it is useful to obtain scale factors. Table 3 presents the values of 12 scale factors, obtained after optimization using the technique outlined above in section 2.

Table 3. Scale Factors Evaluated Using the Optimized Frequency Parameters

coordinate description	scale factor
C=C stretch	0.9916
CF ₂ s-stretch	0.9775
CH ₂ s-stretch	0.9786
CF ₂ a-stretch	0.9729
CH ₂ a-stretch	0.9724
CF ₂ sciss	0.9825
CH ₂ sciss	0.9991
CF ₂ rock	0.9819
CH ₂ rock	1.0131
CF ₂ o.p. wag	0.9129
CH ₂ o.p. wag	1.0232
C=C twist	0.9836

Table 4. Harmonic and Fundamental Frequencies (cm^{-1}) of 1,1-Difluoroethylene: Anharmonic Frequencies Obtained by CVPT2 and CVPT4 with an Anharmonic PES (MP2/cc-pVTZ Model), after Optimization of the Predicted Harmonic Frequencies To Fit CVPT4-Based Fundamental Frequencies to the Observed Values

mode	assignment, approximate	harmonic MP2/cc-pVTZ	difference ^a	harmonic, optimized	difference ^b	anharmonic CVPT2	difference ^c	anharmonic CVPT4	observed, gas phase ^d
A ₁									
ν_1	CH ₂ s-stretch	3249.6	−38.6	3211.0	−156.9	3054.1	3.7	3057.8	3057.8
ν_2	C=C stretch	1786.4	−11.8	1774.6	−48.0	1726.6	1.7	1728.3	1728.3
ν_3	CH ₂ sciss	1425.0	−2.4	1422.6	−64.9	1357.7	1.2	1358.9	1358.9
ν_4	CF ₂ s-stretch	950.3	−8.2	942.1	−15.6	926.5	−0.9	925.6	925.6
ν_5	CF ₂ sciss	559.3	−5.1	554.2	−4.5	549.7	0.0	549.7	549.7
A ₂									
ν_6	C=C twist	731.8	−6.0	725.8	−17.6	708.2	0.0	708.2	708.2
B ₁									
ν_7	CH ₂ as-stretch	3363.7	−47.7	3316.0	−141.7	3174.3	1.3	3175.6	3175.6
ν_8	CF ₂ as-stretch	1350.8	−14.0	1336.8	−35.8	1301.0	0.4	1301.4	1301.4
ν_9	CH ₂ rock	972.4	0.4	972.8	−19.2	953.6	0.3	953.9	953.9
ν_{10}	CF ₂ rock	441.5	−3.7	437.8	−1.7	436.1	1.0	437.1	437.1
B ₂									
ν_{11}	CH ₂ o.p. wag	814.2	6.5	820.7	−21.9	798.8	3.3	802.1	802.1
ν_{12}	CF ₂ o.p. wag	647.8	−29.2	618.6	−9.3	609.3	0.2	609.5	609.5

^aDifferences between optimized and original harmonic frequencies. ^bDifferences between anharmonic and (optimized) harmonic frequencies, equivalent to the anharmonic correction. ^cDifferences between the fourth (CVPT4) and second (CVPT2) orders. ^dReference 1.

Table 5. Comparison of Harmonic Frequencies (cm^{-1}) for 1,1-Difluoroethylene: Different Levels of Quantum Mechanical Theory and “Semi-experimental” Values, Found by Fitting CVPT4 Theoretical Fundamental Frequencies to Observed Ones^a

normal mode	MP2/cc-pVTZ (1)	CCSD(T)/cc-pVTZ (2)	CCSD(T)/cc-pVQZ (3)	CCSD(T)/aug-cc-pVTZ (4)	optimized, CVPT4 (5)	difference, (2) − (5)	difference, (3) − (5)
A ₁							
ω_1	3249.6	3210.6	3207.9	3202.6	3211.0	0.5	3.1
ω_2	1786.4	1778.2	1775.9	1768.4	1774.6	−3.6	−1.3
ω_3	1425.0	1422.4	1416.0	1412.8	1422.6	0.2	6.6
ω_4	950.3	942.6	940.9	934.4	942.1	−0.5	1.2
ω_5	559.3	554.8	554.3	548.4	554.2	−0.6	−0.1
A ₂							
ω_6	731.8	723.2	722.9	714.6	725.8	2.7	3.0
B ₁							
ω_7	3363.7	3317.1	3317.4	3308.9	3316.0	−1.1	−1.4
ω_8	1350.8	1354.2	1340.2	1329.5	1336.8	−17.3	−3.4
ω_9	972.4	972.5	968.8	966.7	972.8	0.3	4.0
ω_{10}	441.5	437.8	435.5	433.0	437.8	0.0	2.3
B ₂							
ω_{11}	814.2	815.6	814.4	810.1	820.7	5.1	6.3
ω_{12}	647.8	624.5	622.7	613.0	618.6	−5.9	−4.1
mean						$\bar{\Delta} = -0.1$	$\bar{\Delta} = 0.2$

^aReference 1.

The only scale factor that significantly deviates from the unity is for the CF₂ out-of-plane wagging coordinate (0.9129). All the others deviate by about 1%–2%.

The results of fitting the CVPT fundamental frequencies to observed vibrational band centers are presented in Table 4. This table presents the MP2/cc-pVTZ harmonic frequencies, the second- and fourth-order CVPT fundamentals, and contributions of the particular step with respect to the previous one. The fitting procedure corrects the original MP2/cc-pVTZ harmonic frequencies to differ from the calculated values by less than −1.4% with the exception ν_{12} , which differs by −4.5%. It is evident that the maximum fourth-order correction (3.66 cm^{-1}) is about 40 times smaller than the corresponding second-order one (156.87 cm^{-1}). The downward progression from the

second-order to fourth-order corrections is evidence that the perturbation theory converges well.

The main emerging question is whether or not the values of fitted harmonic frequencies are physically meaningful. They are obtained on the assumptions that both the anharmonic part of the potential function and the method of calculation of fundamental frequencies are correct. In principle, experimental values of harmonic frequencies can be obtained from purely experimental data, if parameters of Dunham-type expansion (both harmonic frequencies and anharmonic constants) are fitted to experimental frequencies. For a molecule of the size of 11DFE it is nearly impossible to solve the corresponding inverse problem unambiguously, as it is necessary to fit not only the anharmonic constants but also parameters of the resonance-affected Hamiltonian.⁵⁰ The remaining option is to compare

Table 6. Fundamental Vibration Frequencies (cm^{-1}) of 1,1-Difluoroethylene, Obtained by CVPT4 with the Anharmonic PES (MP2/cc-pVTZ Model) and with Substitution of Harmonic Frequencies by the Values Predicted by the CCSD(T)/cc-pVTZ and CCSD(T)/cc-pVQZ Quantum Mechanical Models (Comparison with the Corresponding Observed Values)

mode	MP2/cc-pVTZ	error ^a	ω , from CCSD(T)/cc-pVTZ	error ^a	ω , from CCSD(T)/cc-pVQZ	error ^a	observed, gas phase ^b
A ₁							
ν_1	3088.3	30.5	3059.0	1.2	3053.2	−4.6	3057.8
ν_2	1743.4	15.1	1735.0	6.7	1729.1	0.8	1728.3
ν_3	1366.6	7.7	1358.2	−0.7	1352.4	−6.5	1358.9
ν_4	934.7	9.1	926.3	0.7	924.4	−1.3	925.6
ν_5	555.0	5.3	550.3	0.6	549.8	0.1	549.7
A ₂							
ν_6	717.0	8.8	705.6	−2.6	705.1	−3.1	708.2
B ₁							
ν_7	3226.8	51.2	3176.7	1.1	3176.0	0.4	3175.6
ν_8	1318.2	16.8	1314.7	13.3	1304.3	2.9	1301.4
ν_9	954.7	0.8	953.7	−0.2	949.8	−4.1	953.9
ν_{10}	441.5	4.4	437.1	0.0	434.8	−2.3	437.1
B ₂							
ν_{11}	798.3	−3.8	797.0	−5.1	795.7	−6.4	802.1
ν_{12}	639.2	29.7	615.6	6.1	613.6	4.1	609.5
mean		$\bar{\Delta} = 15.3$		$\bar{\Delta} = 3.3$		$\bar{\Delta} = 3.1$	

^aThe error of the method in the previous (left) column with respect to the observed frequencies. ^bReference 1.

the fitted harmonic frequencies with the corresponding ab initio quantum-mechanical counterparts, which are readily available from analytic Hessians.

Table 5 presents the harmonic frequencies obtained by four ab initio models (including our “basic” MP2/cc-pVTZ model) plus “semi-experimental” values, obtained by fitting harmonic frequencies within CVPT2/CVPT4 anharmonic methods. The MP2/cc-pVTZ model substantially overestimates the values of the C–H stretch frequencies ($\Delta\omega_1 = 38.6 \text{ cm}^{-1}$, $\Delta\omega_7 = 47.7 \text{ cm}^{-1}$) and the CF₂ out-of-plane frequency ($\Delta\omega_{12} = 29.2 \text{ cm}^{-1}$). The frequencies for the CCSD(T)/cc-pVTZ and CCSD(T)/cc-pVQZ models are more-or-less close to each other with the exception of the CF₂-asym-stretch frequency ω_8 , which is overestimated with the cc-pVTZ basis set by 17.3 cm^{-1} . Using the cc-pVQZ basis set decreases this discrepancy to only 3.4 cm^{-1} . Overall, the cc-pVTZ basis set produces a slightly smaller average error of 0.13%, whereas cc-pVQZ produces a similar error of 0.15%, but the maximum error is 6.7 cm^{-1} , less than for the cc-pVTZ basis set. The “augmented” basis set aug-cc-pVTZ causes lowering of all frequencies by -7.6 cm^{-1} on average, the reason for which needs further study.

The most interesting and important conclusion from Table 5 follows from the juxtaposition of ab initio frequencies obtained by the CCSD(T) method and the cc-pVTZ and cc-pVQZ basis sets with the “semi-experimental” harmonic frequencies. As shown in column 6 in Table 5, the differences between CVPT4 optimized “semi-experimental” values and CCSD(T)/cc-pVTZ ones are less than 0.6 cm^{-1} for six fundamentals (ν_1 , ν_3 , ν_4 , ν_5 , ν_9 , ν_{10}) of twelve. Of the remaining six only one (ν_8) has a deviation as large as 17.3 cm^{-1} , whereas for the five remaining ones the deviations are less than 6 cm^{-1} . The problematic fundamental (ν_8) belongs to the CF₂-asym-stretch vibration. However, applying the bigger cc-pVQZ basis set lowers the discrepancy to 3.4 cm^{-1} . The other frequencies are nevertheless reproduced a little worse, but the average error is about the same as with the cc-pVTZ basis set.

Good agreement between harmonic frequencies, obtained by two conceptually different methods (perturbation theory with fitting to experimental data on one hand, and purely ab initio

values, not directly measurable experimentally for a majority of molecules, on the other hand) is a convincing example of the accuracy achieved. Concordant results are found for the electronic structure theory, which provided the anharmonic potential, and the CVPT method, which is based on a number of a priori assumptions and truncations of series expansions. The result has a number of theoretical consequences. First, a comparable level of accuracy can be expected when the same technique is applied to other molecules of similar size and structure. Second, we obtain a method for validation of quantum mechanical potentials, up to sixth derivatives. Third, the most important conclusion is that the whole chain of theoretical methods and molecular properties now links together in such a way that we can directly measure the intermediate discrepancies and prove that a close interpretation of spectra is possible without empirical corrections.

The level of agreement achieved between the “semi-experimental” values of harmonic frequencies and CCSD(T)/cc-pVTZ counterparts is truly impressive in the light of the study performed in ref 89, where an analysis of several factors affecting the accuracy of harmonic force field calculations of water was presented. In particular, it was found that neglecting higher-order electronic correlation terms for CCSD(T)/cc-pVTZ model was estimated to be 4.7 cm^{-1} , and neglecting relativistic effect introduced an error of 2.2 cm^{-1} . These facts clearly indicate that an effective error compensation can take place for the CCSD(T)/cc-pVTZ model. In the case of calculation of the harmonic frequencies of 11DFE, a similar effect was found in ref 89 for water using the CCSD(T)/aug-cc-pVQZ model chemistry.

Table 6 illustrates what accuracy can be achieved in predicting the fundamentals without any involvement of experimental data by using the “hybrid” scheme. In this method the harmonic frequencies obtained at the higher ab initio level are combined with the rest of the anharmonic potential contributions taken from more economical calculations. This technique is a stricter alternative to transferring scale factors, as it does not employ any empirical information. Table 6 shows the fundamental frequencies, obtained by

Table 7. Observed¹ and Calculated Vibrational States (cm⁻¹) of 1,1-Difluoroethylene

¹² C gas ^a	calculated ^a	sym, polyad, IR intensity ^b	new assignment: dominant states	assignment ^c
Polyad: 16				
3503.1 vw Q	3503.9	A ₁ , 16, 0.08	76% $\nu_4 + 2\nu_8$	
3479.2 vw Q				
3470.4 vw Q	3472.7	A ₁ , 16, 0.12	40% $\nu_2 + \nu_8 + \nu_{10}$ 25% $2\nu_8 + 2\nu_{10}$	$2\nu_8 + 2\nu_{10}$ (A ₁) FR
3456.6 vw Q	3456.9	A ₁ , 16, 0.70	61% $2\nu_2$ 24% $2\nu_8 + 2\nu_{10}$	$2\nu_2$ (A ₁) FR
3451.2 vw Q				
3442.1 vw Q	3442.9	A ₁ , 16, 0.20	32% $\nu_2 + \nu_8 + \nu_{10}$ 22% $\nu_3 + 2\nu_{10} + 2\nu_{12}$	
3440.5 vw Q	3440.9	A ₁ , 16, 0.07	43% $\nu_3 + 2\nu_{10} + 2\nu_{12}$	
Polyad: 14				
3255.9 vw Q	3260.8	A ₁ , 14, 0.02	47% $\nu_3 + \nu_6 + \nu_{10} + \nu_{11}$ 29% $3\nu_6 + \nu_{10} + \nu_{11}$	
3255.9 vw Q	3251.0	A ₁ , 14, 0.03	52% $\nu_3 + 2\nu_9$	
3199.4 vw B	3199.0	B ₁ , 14, 0.02	78% $\nu_8 + 2\nu_9$	$\nu_8 + 2\nu_9$ (B ₁) FR
3175.6 vw B	3175.6	B ₁ , 14, 1.08	86% ν_7	ν_7 (B ₁)
3167.3 vw Q	3167.0	A ₁ , 14, 0.09	42% $\nu_4 + \nu_8 + \nu_9$ 13% $3\nu_6 + \nu_{10} + \nu_{12}$	$\nu_2 + 2\nu_6$
3154.8 vw Q	3155.9	A ₁ , 14, 0.36	19% $\nu_2 + 2\nu_6$ 18% $\nu_8 + \nu_{10} + \nu_{11} + \nu_{12}$ 15% $\nu_2 + \nu_3$	$\nu_8 + \nu_{10} + 2\nu_6$
3111.5 w Q	3111.1	A ₁ , 14, 1.10	18% $\nu_2 + \nu_3$ 17% $\nu_2 + \nu_9 + \nu_{10}$ 17% $\nu_2 + \nu_{11} + \nu_{12}$ 17% $\nu_8 + \nu_9 + 2\nu_{10}$ 16% ν_1	$\nu_2 + \nu_3$
3101.4 w Q	3099.9	A ₁ , 14, 0.87	50% $\nu_2 + \nu_9 + \nu_{10}$	$\nu_2 + \nu_9 + \nu_{10}$
3098.6 w Q	3096.2	A ₁ , 14, 0.57	30% $\nu_3 + \nu_6 + \nu_{10} + \nu_{12}$ 17% $\nu_3 + \nu_8 + \nu_{10}$	$2\nu_5 + \nu_6 + \nu_8$ (B ₂) FR
3085.3 vw Q	3083.3	A ₁ , 14, 0.19	30% $\nu_3 + \nu_8 + \nu_{10}$ 26% $\nu_3 + \nu_6 + \nu_{10} + \nu_{12}$	$\nu_3 + \nu_8 + \nu_{10}$
3057.8 w A	3057.8	A ₁ , 14, 2.79	56% ν_1 34% $\nu_2 + \nu_3$	ν_1 (A ₁) FR P1
3052.2 vw Q	3052.3	B ₁ , 14, 0.004	67% $\nu_5 + \nu_8 + 2\nu_{12}$	$\nu_8 + \nu_9 + \nu_{11}$ (B ₂) FR
3052.2 vw Q	3052.4	B ₁ , 14, 0.002	27% $\nu_6 + \nu_8 + \nu_{10} + \nu_{12}$	
3015.5 vw B	3017.1	B ₁ , 14, 0.12	43% $\nu_2 + \nu_8$ 37% $2\nu_8 + \nu_{10}$	$2\nu_8 + \nu_{10}$ (B ₁) FR
2945.3 vw Q	2947.9	A ₁ , 14, 0.03	57% $\nu_8 + \nu_{10} + 2\nu_{12}$	$\nu_8 + \nu_{10} + 2\nu_{12}$ (A ₁) FR
2932.2 vw Q	2934.1	A ₁ , 14, 0.06	66% $\nu_2 + 2\nu_{12}$	
Polyad: 12				
2945.3 vw Q	2944.3	A ₁ , 12, 0.03	61% $\nu_3 + 2\nu_{11}$	
2831.4 vw Q	2831.0	A ₁ , 12, 0.05	84% $\nu_4 + 2\nu_9$	$\nu_4 + 2\nu_9$ (A ₁)
2777.7 vw Q	2774.2	A ₁ , 12, 0.11	30% $2\nu_3$ 27% $2\nu_6 + \nu_{11} + \nu_{12}$... 6% $\nu_3 + 2\nu_6$	$\nu_3 + 2\nu_6$ (A ₁) FR
2707.3 vw Q	2703.5	A ₁ , 12, 0.16	42% $2\nu_3$ 16% $\nu_3 + 2\nu_6$ 16% $\nu_3 + \nu_{11} + \nu_{12}$	$2\nu_3$ (A ₁) FR
2674.0 vw B	2672.6	B ₁ , 12, 0.09	76% $\nu_2 + \nu_9$	$\nu_2 + \nu_9$ (B ₁) FR
2661.2 vw A	2660.7	A ₁ , 12, 0.86	46% $\nu_4 + \nu_8 + \nu_{10}$ 41% $\nu_2 + \nu_4$	$\nu_4 + \nu_8 + \nu_{10}$ (A ₁) FR
2647.6 vw A	2647.2	A ₁ , 12, 2.23	57% $\nu_2 + \nu_4$	$\nu_2 + \nu_4$ (A ₁) FR
2611.0 vw Q	2612.7	A ₁ , 12, 0.36	44% $\nu_6 + \nu_8 + \nu_{12}$	$\nu_6 + \nu_8 + \nu_{12}$ (A ₁) FR
2592.6 vw A	2593.6	A ₁ , 12, 2.01	71% $2\nu_8$	$2\nu_8$ (A ₁) FR
Polyad: 10				
2534.8 vw Q	2535.2	A ₁ , 10, 0.05	97% $\nu_4 + 2\nu_{11}$?
2513.7 vw Q	2512.4	A ₁ , 10, <10 ⁻⁴	61% $2\nu_5 + 2\nu_6$	$2\nu_9 + \nu_{12}$ (A ₁)
2466.8 vw Q				$\nu_4 + \nu_9 + \nu_{12}$ (A ₂) ?
2427.0 vw Q				C ₂ F ₂
2424.9 vw Q	2425.0	B ₁ , 10, <10 ⁻⁴	98% $\nu_4 + \nu_5 + \nu_9$?

Table 7. continued

^{12}C gas ^a	calculated ^a	sym, polyad, IR intensity ^b	new assignment: dominant states	assignment ^c
Polyad: 10				
2353.6 vw Q	2354.5	A ₁ , 10, 0.03	35% $\nu_4 + \nu_{11} + \nu_{12}$	$\nu_4 + \nu_5 + 2\nu_{10}$ (A ₁) FR ?
2343.4 vw Q	2342.7	B ₁ , 10, 0.002	65% $2\nu_9 + \nu_{10}$	$\nu_8 + \nu_{10} + \nu_{12}$ (B ₂) FR
2335.1 vw Q	2334.7	A ₁ , 10, 0.006	59% $\nu_4 + 2\nu_6$	$\nu_4 + \nu_{11} + \nu_{12}$ (A ₁) FR
2330.5 vw Q				$\nu_2 + \nu_{12}$ (B ₂) FR
2317.5 vw Q	2316.6	A ₁ , 10, 0.09	79% $\nu_4 + \nu_9 + \nu_{10}$	$\nu_4 + \nu_9 + \nu_{10}$ (A ₁) FR
2288.5 vvw Q	2286.5	A ₁ , 10, 0.06	96% $2\nu_4 + \nu_{10}$	$\nu_5 + \nu_8 + \nu_{10}$ (A ₁) FR
2283.1 vw Q	2282.7	A ₁ , 10, 0.08	68% $\nu_3 + \nu_4$	$\nu_3 + \nu_4$ (A ₁) FR
2270.8 vw Q	2271.1	A ₁ , 10, 0.12	89% $\nu_6 + \nu_9 + \nu_{12}$	$\nu_6 + \nu_9 + \nu_{12}$ (A ₁) FR
2250.3 w A	2250.3	A ₁ , 10, 1.48	87% $\nu_8 + \nu_9$	$\nu_8 + \nu_9$ (A ₁) FR
2220.8 vw A ?				?
2220.2 vw Q ?	2219.3	B ₁ , 10, 1.45	87% $\nu_4 + \nu_8$	$\nu_4 + \nu_8$ (B ₁) FR
2162.0 vvw B	2160.7	B ₁ , 10, 0.02	66% $\nu_2 + \nu_{10}$	$\nu_2 + \nu_{10}$ (B ₁) FR
Polyad: 9				
2046.3 vw Q	2049.3	B ₂ , 9, 0.01	55% $\nu_{11} + 2\nu_{12}$	$2\nu_6 + \nu_{12}$ (B ₂) FR
2024.5 vw Q	2023.9	B ₂ , 9, 0.003	57% $2\nu_6 + \nu_{12}$	$\nu_{11} + 2\nu_{12}$ (B ₂) FR ?
2005.7 vw Q	2005.7	B ₂ , 9, 0.002	75% $\nu_6 + \nu_8$	$\nu_6 + \nu_8$ (B ₂) FR
1996.1 vvw Q				
Polyad: 8				
1980.6 vvw Q	1982.2	A ₁ , 8, 0.04	40% $\nu_5 + \nu_{11} + \nu_{12}$ 28% $\nu_5 + 2\nu_6$... 10% $2\nu_5 + 2\nu_{10}$	$2\nu_5 + 2\nu_{10}$ (A ₁) ?
1908.0 w A	1908.9	A ₁ , 8, 0.30	57% $\nu_3 + \nu_5$	$2\nu_9$ (A ₂)
1908.0 w A	1906.9	A ₁ , 8, 4.10	81% $2\nu_9$	$\nu_4 + \nu_9$ (B ₁)
1878.4 w B	1878.5	B ₁ , 8, 0.79	100% $\nu_4 + \nu_9$	$\nu_5 + 3\nu_{10}$ (B ₁)
$\nu_5 + 3\nu_{10}$ (B ₁)				$2\nu_4$ (A ₁)
1848.5 w A	1847.7	A ₁ , 8, 1.38	100% $2\nu_4$	$\nu_4 + 2\nu_{10}$ (A ₁) FR
1803.2 vw Q	1803.8	A ₁ , 8, 0.09	96% $\nu_4 + 2\nu_{10}$	$\nu_8 + \nu_{10}$ (A ₁) FR
1741.8 vs A	1741.3	A ₁ , 8, 103.9	51% ν_2 39% $\nu_8 + \nu_{10}$	ν_2 (A ₁) FR
1728.3 vs A	1728.3	A ₁ , 8, 147.6	59% ν_2 37% $\nu_8 + \nu_{10}$	
Polyad: 6				
1610.9 m A	1611.1	A ₁ , 6, 21.25	98% $2\nu_{11}$	$2\nu_{11}$ (A ₁) ?
1541.5 vw Q				
1504.4 vw B	1503.2	B ₁ , 6, 0.01	97% $\nu_5 + \nu_9$	$\nu_6 + \nu_{11}$ (B ₁)
1504.4 vw B	1499.0	B ₁ , 6, 0.23	100% $\nu_6 + \nu_{11}$	$\nu_4 + \nu_5$ (A ₁)
1472.1 vw A	1472.6	A ₁ , 6, 0.27	100% $\nu_4 + \nu_5$	$2\nu_6$ (A ₁) FR, DDR
1431.0 vw Q	1431.8	A ₁ , 6, 0.49	44% $\nu_{11} + \nu_{12}$ 30% $2\nu_6$	
1412.9 w A	1412.0	A ₁ , 6, 1.80	59% $2\nu_6$ 34% $\nu_{11} + \nu_{12}$	$\nu_{11} + \nu_{12}$ (A ₁) FR, DDR
1393.0 vw Q	1391.8	A ₁ , 6, 0.22	85% $\nu_9 + \nu_{10}$	$\nu_9 + \nu_{10}$ (A ₁) FR
1363.6 wm B	1363.6	B ₁ , 6, 5.35	98% $\nu_4 + \nu_{10}$	$\nu_4 + \nu_{10}$ (B ₁) FR
1358.9 wm Q	1358.9	A ₁ , 6, 0.27	69% ν_3 11% $\nu_{11} + \nu_{12}$	ν_3 (A ₁) FR
1319.1 s B	1319.4	B ₁ , 6, 29.1	86% $\nu_6 + \nu_{12}$ 13% ν_8	$\nu_6 + \nu_{12}$ (B ₁) FR
1319.1 s B	1318.0	B ₁ , 6, 1.10	100% $3\nu_{10}$	
1301.4 vs B	1301.4	A ₁ , 6, 189.7	84% ν_8 14% $\nu_6 + \nu_{12}$	ν_8 (B ₁) FR
1244.2 vvw Q				?
1218.0 vw A	1219.3	A ₁ , 6, 2.72	100% $2\nu_{12}$	$2\nu_{12}$ (A ₁) impurity? ?
1180.9 vvw Q				
1178.3 vvw Q				
Polyad: 5				
1145.6 vw Q	1145.4	B ₂ , 5, 0.002	100% $\nu_6 + \nu_{10}$	$\nu_6 + \nu_{10}$ (B ₂)
1048.9 vvw Q				?
1046.6 vw Q	1047.0	A ₂ , 5, <10 ⁻⁴	100% $\nu_{10} + \nu_{12}$	$\nu_{10} + \nu_{12}$ (A ₂)

Table 7. continued

¹² C gas ^a	calculated ^a	sym, polyad, IR intensity ^b	new assignment: dominant states	assignment ^c
Polyad: 4				
LA: 988.2	987.4	B ₁ , 4, 0.02	100% $\nu_5 + \nu_{10}$	
953.9 m B	953.9	A ₂ , 4, 15.92	100% ν_9	ν_9 (B ₁)
925.6 s A	925.8	A ₁ , 4, 65.71	100% ν_4	ν_4 (A ₁)
882.2 vw Q	(882.2) ^d		$(\nu_6 + \nu_{12}) - \nu_{10}$	$\nu_6 + \nu_{12} - \nu_{10}$ (A ₁)
864.0 vw Q	(864.3)		$\nu_8 - \nu_{10}$	$\nu_8 - \nu_{10}$ (A ₁)
821.8 ms Q	(822.3)		$(\nu_{11} + \nu_{12}) - \nu_{12}$	$\nu_{11} + \nu_{12} - \nu_{12}$ (B ₂)
Polyad: 3				
802.1 s C	802.1	B ₂ , 3, 74.17	100% ν_{11}	ν_{11} (B ₂)
748.9 w Q	(749.4)		$\nu_3 - \nu_{12}$	$\nu_3 - \nu_{12}$ (B ₂)
743.6 vw Q				?
708.2 vvw Q	708.2	A ₂ , 3, <10 ⁻⁴	100% ν_6	ν_6 (A ₂)
629.1 w C	(629.7)		$2\nu_6 - \nu_{11}$	$2\nu_6 - \nu_{11}$ (B ₂)
609.5 w C	609.5	B ₂ , 3, 0.68	100% ν_{12}	ν_{12} (B ₂)
Polyad: 2				
549.8 m A	549.8	A ₁ , 2, 4.90	100% ν_5	ν_5 (A ₁)
437.1 wm B	437.1	B ₁ , 2, 0.98	100% ν_{10}	ν_{10} (B ₁)

^aThe IR frequency and relative intensity data are all taken from ref 1. Fundamentals are in boldface. LA = liquid argon. ^bThe units of calculated IR intensities are given in km/mol. ^cReference 1. Values in bold italic are errant assignments. ^dValues of difference bands in parentheses are calculated from assignments in ref 1.

CVPT4 both with purely the MP2/cc-pVTZ “semi-diagonal” sextic potential and after substitution of harmonic frequencies with ones obtained at the CCSD(T)/cc-pVTZ and CCSD(T)/cc-pVQZ levels. The MP2 method does not look adequate as the errors in ν_1 , ν_7 , and ν_{12} are too big, reaching ~ 50 cm⁻¹ for ν_7 . Taking the harmonic frequencies from the CCSD(T) method, for both basis sets (cc-pVTZ and cc-pVQZ) dramatically decreases the average error. The fit for CCSD(T)/cc-pVTZ looks almost ideal, with seven predicted fundamentals deviating from observed values by <1.2 cm⁻¹. However, the picture is slightly spoiled by ν_8 , which belongs to the CF₂-as-stretch vibration, which deviates by 13.3 cm⁻¹. The cc-pVQZ fundamentals produce the smallest average error, mainly due to significantly improving ν_8 , whereas the fit for the other fundamentals looks slightly less impressive than for the cc-pVTZ basis set.

A main result of this paper is summarized in Table 7, where all observed gas-phase experimental frequencies are juxtaposed with calculated ones and with the previous assignments.¹ The advantages of the new vibrational analysis in comparison with the previous one are as follows: (a) after defining the form of the polyad vector, which required some manual participation, all the remaining calculations were performed in a fully “black-box” manner; (b) vibrational states are presented as linear combinations of the basis harmonic oscillator zero-order states, so that the share of each basis function is presented in percent; (c) CVPT reliably predicts not only the frequencies but also IR (with possible extension to Raman) intensities for all transitions, taking into account the mixing of vibrational states; (d) using the polyad numbers ensures breaking down the Hamiltonian into isolated blocks.

We summarize the most interesting features of the interpretation of the spectrum, itemized by polyad numbers. At this point it is worthwhile to note that each polyad puts together all possible states with the same value of PQN, which in turn are linear combinations of the zero-order states characterized by quantum numbers of the corresponding basis functions. Because we need to establish a correspondence between observed band centers and anharmonic states,

omitting the transitions with negligible infrared intensities reduces the number of states of interest by a factor of 10. As seen from Table 2, the polyads with odd numbers contain only the A₂ and B₂ symmetry species. The A₂ species are IR inactive, and the B₂ transitions tend to be weak, except for the one fundamental of this symmetry. The full analysis of assignment of observed bands and interesting features are presented below in detail.

4.1. Polyads 2–5 (437–1146 cm⁻¹). In these polyads, there are seven fundamental transitions (ν_4 , ν_5 , ν_6 , ν_9 , ν_{10} , ν_{11} , ν_{12}) and two observable binary combination bands ($\nu_5 + \nu_{10}$, $\nu_{10} + \nu_{12}$). All of these states are “pure”, i.e., free from any significant resonance interactions. Other binary combination bands have negligible intensity.

4.2. Polyad 6 (1178–1611 cm⁻¹). This polyad has two fundamentals (ν_3 , ν_8), three first overtones ($2\nu_6$, $2\nu_{11}$, $2\nu_{12}$), one second overtone ($3\nu_{10}$), and seven ($\nu_4 + \nu_5$, $\nu_4 + \nu_{10}$, $\nu_5 + \nu_9$, $\nu_6 + \nu_{11}$, $\nu_6 + \nu_{12}$, $\nu_9 + \nu_{10}$, $\nu_{11} + \nu_{12}$) binary combination bands that are observable. There is a weak 1–11 Fermi resonance between $\nu_6 + \nu_{12}$ and ν_8 , with level shifts of about 3 cm⁻¹. Another 1–11 Fermi resonance between $\nu_{11} + \nu_{12}$ and ν_3 is much stronger, and the mixed states include $2\nu_6$. The lower energy fundamental level ν_3 (1358.9 cm⁻¹) is shifted downward by ~ 25 cm⁻¹ after diagonalization. Assignment of the perturbed fundamental transition in the region from 1300 to 1400 cm⁻¹ has been a problem for many years.¹ The recent interpretation¹ is reinforced and is revised somewhat in the present work.

The combination level $\nu_{11} + \nu_{12}$ is shifted upward by ~ 18 cm⁻¹. The observed pair of frequencies 1431.0 vw Q and 1412.9 w A is a good example of a 2–11 Darling–Dennison resonance between states $2\nu_6$ and $\nu_{11} + \nu_{12}$. The original interpretation assigned the lower frequency to $\nu_{11} + \nu_{12}$,¹ whereas our calculation swaps the assignments and accurately predicts the positions of both bands and the difference in intensities: 1431.8 cm⁻¹, 0.49 km/mol with 44% share for $\nu_{11} + \nu_{12}$ (1431.0 vw Q), and 1412.0 cm⁻¹, 1.80 km/mol with 59% share for $2\nu_6$ (1412.9 w A). Although, in general, the Darling–Dennison resonance is a common phenomenon, in the analyzed spectrum there are no other “pure” spectroscopic

manifestations of this effect for 11DFE in the range up to 3500 cm^{-1} .

It is interesting to note that using the standard unadjusted K_{DD} (2–11) formula²⁷ produces the value of 40.46 cm^{-1} , whereas the adjusted formula (with removal of Fermi-resonance terms)^{27,56} yields 5.89 cm^{-1} . CVPT4 gives the value of $K_{\text{DD}} = 6.70 \text{ cm}^{-1}$, and the corresponding matrix element is 2.37 cm^{-1} . This value of the matrix element predicts the splitting of 19.8 cm^{-1} between the resonating states $2\nu_6$ and $\nu_{11} + \nu_{12}$, a result in a good agreement with the experimental value of 18.1 cm^{-1} .

4.3. Polyad 8 (1728–1981 cm^{-1}). This polyad contains seven observed bands, which include one fundamental (ν_2), two overtones ($2\nu_4$, $2\nu_9$), three binary combination bands ($\nu_3 + \nu_5$, $\nu_4 + \nu_9$, $\nu_8 + \nu_{10}$), and three more complex mixed states, $\nu_5 + \nu_{11} + \nu_{12}$, $\nu_4 + 2\nu_{10}$, and $\nu_5 + 2\nu_6$. The strong Fermi resonance between ν_2 and $\nu_8 + \nu_{10}$, which gives bands of equal intensity, is confirmed.¹ The observed band 1980.6 vw Q was previously assigned to $2\nu_5 + 2\nu_{10}$,¹ whereas it is a triple combination $\nu_5 + \nu_{11} + \nu_{12}$. There is a strong repulsion between zero-order states, participating in levels 1980.6 vw Q (theoretical shift -24 cm^{-1}) and 1908.0 w A (shift $+17 \text{ cm}^{-1}$). The big shifts after diagonalization occur due to complex interactions between states $\nu_3 + \nu_5$, $\nu_5 + 2\nu_6$, and $\nu_5 + \nu_{11} + \nu_{12}$. This case is an interesting example of a resonance that cannot be described simply as a Fermi or Darling–Dennison one. The predicted close pair of frequencies 1908.9 and 1906.9 cm^{-1} is assigned to $\nu_3 + \nu_5$ and $2\nu_9$, respectively, whereas only one band is observed at 1908.0 w A. It appears that the weaker (0.3 km/mol) combination band $\nu_3 + \nu_5$ is “hiding” in the rotational structure of the much stronger (4.1 km/mol) overtone $2\nu_9$, so that the same observed frequency is assigned to them in Table 7.

4.4. Polyad 10 (1996–2535 cm^{-1}). This polyad spans about 650 cm^{-1} and mostly includes states with total quanta of more than two, but there are two relatively more intense ($\sim 1.5 \text{ km/mol}$ each) binary combination bands 2250.3 w A ($\nu_8 + \nu_9$) and 2220.2 vw Q ($\nu_4 + \nu_8$). The transition to the former state $\nu_8 + \nu_9$ shares intensity with a “dark” state transition $\nu_6 + \nu_9 + \nu_{12}$ (2270.8 vw Q), which otherwise would have been unobservable. This resonance is weak and can be considered as a third-order one. There are two other weaker binary combination bands at 2162.0 vw B ($\nu_2 + \nu_{10}$) and 2283.1 vw Q ($\nu_3 + \nu_4$). There are a number of reassignments in the region from 2285 to 2515 cm^{-1} . Possible mistakes in the previous assignment¹ can be explained by the complex character of mixed states and difficulties in evaluation of interaction matrix elements.

4.5. Polyad 12 (2592–2945 cm^{-1}). This polyad spans about 850 cm^{-1} and does not include any basis functions corresponding to fundamental transitions, so that there is no manifestation of the first-order (1–11 and 1–2) Fermi resonances. In fact, all observed resonances in this polyad are of the third order and higher. A detailed description can be found in Table 7.

4.6. Polyad 14 (2932–3256 cm^{-1}). This polyad contains two C–H stretching fundamentals, ν_1 and ν_7 , and is characterized by a high density of modestly intense transitions. Needless to say, there are many resonances and intensity gains by “dark” states. This polyad also contains two binary combination bands $\nu_2 + \nu_8$, $\nu_2 + \nu_3$. The latter state ($\nu_2 + \nu_3$) is heavily mixed with a number of states, and the transition gains intensity from ν_1 , which is shifted by -23 cm^{-1} in the theoretical analysis. This example is a classic case of Fermi

resonance, although the “dark” counterpart $\nu_2 + \nu_3$ is severely mixed with other states, being spread through states over the range of $\sim 100 \text{ cm}^{-1}$ from 3057 to 3156 cm^{-1} and is not strongly shifted after diagonalization (-5 cm^{-1}). Whereas ν_1 is strongly influenced by resonances, ν_7 is confirmed as being essentially free of resonances at 3176 cm^{-1} .

4.7. Polyads 15–28. These polyads cover the range from 3050 to 7750 cm^{-1} and do not contain any fundamentals. Most of these transitions have low or nil intensity. However, three first overtones (for ν_1 , ν_2 , and ν_7) and twenty-two binary combination bands are located there.

In the Tables S1 and S2 (Supporting Information) the detailed interpretation of observed first overtones and binary combination bands can be found.

In Table 7, the agreement between the new results for the analysis of the IR spectrum of 11DFE and the previous interpretation of McKean et al.¹ is fairly good even though the prior investigation depended on extensive work “by hand”, including the local investigation of resonance multiplets. Where the previous assignments differ from the new, they are shown in bold italic type in column 5 in Table 7. The biggest discrepancy is for the complex Fermi resonance multiplet involving ν_1 . A number of weak bands previously unassigned have now been assigned. The predictions of IR intensities for combination bands are new and are generally in acceptable agreement with experiment. For weak bands, in general, more latitude must be given to the comparisons between predicted and observed intensities. Nonetheless, the agreement between observations and predictions for the intensities of all the bands is acceptable. Symmetry-distinguishing band shapes were unavailable for a number of bands, where only Q branches were observed. All considered, the new calculations are a significant advance over the previous work and strengthen the interpretation of the many bands in the IR spectrum of 11DFE. The automation of the new calculations is a great advance over the time-consuming and potentially error-prone work invested in the previous analysis.

5. CONCLUSIONS

Both the traditional VPT2 perturbation theory treatment and the CVPT method require an additional matrix diagonalization. For this purpose, it is necessary to choose a sufficiently wide set of basis functions and to evaluate the precise values of resonance couplings. In comparison with the traditional VPT2 technique, the CVPT method provides the more systematic search for resonance coefficients and the evaluation of the coupling coefficients. However, the proper basis set choice remains unresolved. It is the polyad technique that solves this remaining problem, at least for the six-atomic 1,1-difluoroethylene molecule. For this molecule the polyad formula was obtained in straightforward manner in the form $P = 14(\nu_1 + \nu_7) + 8\nu_2 + 6(\nu_3 + \nu_8) + 4(\nu_4 + \nu_9) + 3(\nu_6 + \nu_{11} + \nu_{12}) + 2(\nu_5 + \nu_{10})$, where the ν_i are quantum numbers.

The knowledge of the form of the polyad quantum number allows immediate classification of both the basis vectors and vibrational states. If all the resonance vectors are strictly orthogonal to the polyad vector and the polyad formula has no zero coefficients, the Hamiltonian matrix acquires the block-diagonal form, which ensures completeness and usually small sizes for the required basis sets. Under such circumstances the CVPT solution can be considered equivalent to the variational method with the provision that it relates to the corresponding order of perturbation theory.

The method we employed allows a reliable estimation of harmonic frequencies ω_e , which have a clear physical meaning and can be directly compared to ones obtainable from quantum mechanical harmonic force fields. The set of the “semi-experimental” harmonic frequencies was obtained by fitting CVPT4 theoretical fundamental frequencies to observed fundamental transitions. By comparing them to the theoretical quantum-mechanical counterparts, evaluated at different levels of theory, we have found that the best match occurs for the following quantum-mechanical models: CCSD(T)/cc-pVTZ and CCSD(T)/cc-pVQZ. Adding “aug-” to the cc-pVTZ basis set makes the correspondence worse. A very good match between the CVPT4 “semi-experimental” harmonic frequencies and their theoretical quantum-mechanical counterparts has several important theoretical consequences. First, the results confirm that the “hybrid” quantum mechanical force field obtained by adding higher PES terms (cubic to sextic) from the MP2/cc-pVTZ model to quadratic ones obtained at the higher CCSD(T)/cc-pVTZ level is good enough to predict the anharmonic vibrational spectrum with high accuracy by applying the CVPT4 method. This formulation allows a confident interpretation of the experimental spectrum without any empirical adjustments. Second, the quality of predictions of the canonical van Vleck perturbation theory at the fourth order (CVPT4) in the presence of multiple resonances can be considered to be high, comparable to the quality of the direct variational method.⁹⁰ However, unlike the variational method, the CVPT produces anharmonic second-order and fourth-order spectroscopic constants x_{rs} and y_{rst} of the Dunham-type expansion, along with resonance coupling constants. Third, the very good match between fitted harmonic frequencies and quantum mechanical ones, obtained at the CCSD(T)/cc-pVTZ level and the diminished agreement for the frequencies obtained at CCSD(T)/aug-cc-pVTZ level can be a sign that in the CCSD(T)/cc-pVTZ model there is probably some error compensation effect. The regularity in the signs of errors corroborates this assumption.

The general conclusion is that for the molecules of the size of 1,1-difluoroethylene, containing C=C and C—F bonds, application of the CVPT4 in combination with a sextic “hybrid” quantum-mechanical force field works very well. The method is enhanced by the polyad quantum number technique and the calculation of anharmonic IR intensities. As a result, a complete interpretation of vibrational spectra is possible. It is shown that CVPT4 is substantially superior to the more traditional VPT2 method, mainly due to the general theoretical problem of finding the correct values of resonance coupling coefficients in the latter method.

■ ASSOCIATED CONTENT

■ Supporting Information

Two tables with a complete listing of the predicted and observed first overtones and binary combination bands of 1,1-difluoroethylene are presented. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*Tel: 7 (495) 939-2950. E-mail: sergeyk@phys.chem.msu.ru.

Notes

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