

**How accurately can perturbative and variational vibrational models predict
the fundamental frequencies of dihalomethanes?**

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Abstract

Three dihalogenated methane derivatives (CH_2F_2 , CH_2FCl and CH_2Cl_2) were used as model systems to compare and assess the accuracy of two different approaches for predicting observed fundamental frequencies: canonical operator Van Vleck vibrational perturbation theory (CVPT) and vibrational configuration interaction (VCI). For convenience and consistency, both methods employ the Watson Hamiltonian in rectilinear normal coordinates, expanding the potential energy surface (PES) as a Taylor series about equilibrium, and constructing the wavefunction from a harmonic oscillator product basis. At the highest levels of theory considered here, fourth-order CVPT and VCI in a harmonic oscillator basis with up to 10 quanta of vibrational excitation in conjunction with a 4-mode representation sextic force field (SFF-4MR), the agreement between computed fundamentals is closer than 0.3 cm^{-1} on average, with a maximum difference of 1.7 cm^{-1} . The major remaining accuracy-limiting factors are the accuracy of the underlying electronic structure model, followed by the incompleteness of the PES expansion. Nonetheless, computed and experimental fundamentals agree to within 5 cm^{-1} , with an average difference of 2 cm^{-1} , confirming the utility and accuracy of both theoretical models. One exception to this rule is the formally IR-inactive but weakly allowed through Coriolis-coupling H-C-H out-of-plane twisting mode of dichloromethane, whose spectrum we therefore revisit and reassign. We also investigate convergence with respect to order of CVPT, VCI excitation level and order of PES expansion, concluding that premature truncation substantially decreases accuracy, although VCI(6)/SFF-4MR results are still of acceptable accuracy, and some error cancellation is observed at CVPT2 using a quartic force field (QFF).

Keywords: Canonical Van Vleck Perturbation Theory, Vibrational Configuration Interaction, Sextic Force Field, Halogenated Methanes

1. Introduction

Fluoro- and chloro-substituted derivatives of methane play major roles in the chemistry and spectroscopy of the Earth's atmosphere and thus have attracted considerable attention from researchers. In particular, the vibrational and ro-vibrational spectra of difluoromethane,[1-8] fluorochloromethane [9-14] and dichloromethane [15-23] have been measured and assigned by group frequency theoretical analysis and parameterizing model Hamiltonians. Their equilibrium semi-experimental structures have also been obtained.[24] Recently, the experimental vibrational spectroscopy studies of these molecules have been supplemented by *ab initio* anharmonic computational models.[7,12,25,26] These models explicitly map the structural and energetic information contained in *ab initio* computed molecular potential energy and dipole moment surfaces to spectroscopically observable quantities, such as transition energies and intensities, by solving the nuclear vibrational Schrödinger equation.

Although *ab initio* nuclear vibrational models are powerful and flexible tools for interrogating the spectroscopic signature of halomethanes, they typically do not achieve “spectroscopic accuracy” ($\sim 1 \text{ cm}^{-1}$) in predicting transition energies.[27-29] This deficiency is due to a superposition of underlying approximations, including: (1) the level of *ab initio* electronic structure theory used to construct the potential energy surface (PES); (2) the form and extent of the PES representation; and (3) the approach taken to solving the nuclear vibrational Schrödinger equation. In certain cases, fortuitous error cancellation effects even for an economic DFT model can lead to a rather good agreement of a few cm^{-1} between predicted and observed vibrational states.[30]

We aim to disentangle these sources of error by assessing the convergence behaviour of nuclear vibrational structure models and independently estimating the error due to incomplete convergence in the electronic structure model underpinning the PES. Dihalomethanes are convenient model systems. As semi-rigid molecules with nine degrees of

vibrational freedom, they are sufficiently complex that they exhibit non-trivial vibrational structure but simple enough that numerically stable sextic potential energy surfaces can be computed. Additionally, high quality spectroscopic reference data are available for most of the vibrational transitions.[1-23]

There are two major classes of quantum mechanical *ab initio* “black-box” nuclear vibrational methods that can, in principle, converge to exact solutions within the single minimum conformer approximation; vibrational perturbation theory and vibrational configuration interaction or coupled cluster theory. Perturbation theory can approach the exact solution to the nuclear vibrational Schrödinger equation if the perturbative expansion is convergent and not prematurely truncated. The classic Rayleigh-Schrödinger formulation of vibrational perturbation theory (RSPT) [31-33] yields simple closed-form second-order energy expressions, from which it is straightforward to identify and variationally account for divergent (resonant) terms.[34,35] However, it is much harder to derive closed-form energy expressions as well as identify and appropriately account for vibrational resonances at fourth order.[36-38] The formidable algebraic and computational complexity of RSPT4 has prevented its general implementation to date. In principle, it is possible to find an RSPT solution at very high orders by resummation of divergent series,[39-42] but such approaches are rather scarce.

Therefore, we turn to the canonical van Vleck operator perturbation theory (CVPT) formalism,[33,43-56] in which the nuclear vibrational problem is solved by numerically manipulating the Hamiltonian operator [50,55-57] rather than pursuing purely analytical solutions.[33] In CVPT, a series of unitary transformations is applied to quasi-diagonalize the Hamiltonian to a given order, excluding blocks of strongly-coupled and degenerate terms that must be treated variationally. The required transformation operators are derived using perturbation theory, expanding both the transformation operator and the original and target

Hamiltonians in powers of a perturbation parameter, and then equating terms with like powers. The original Hamiltonian must be expressed as the sum of a dominant zeroth-order, analytically solvable component and a series of higher order correction terms and is particularly efficient using the Watson Hamiltonian with the PES expanded as a Taylor series about equilibrium in rectilinear normal mode coordinates. Like for RSPT, it is feasible to apply CVPT to higher than second order.[50,55-57]

In vibrational configuration interaction (VCI) [58-65] and vibrational coupled cluster theory,[66-68] there is a substantial freedom of choice in the potential energy surface representation and form of the vibrational wavefunction, which in turn affords a much higher degree of flexibility in choice of vibrational Hamiltonian and coordinate system.[69-71]

For example, (a) the Hamiltonian may be formulated in rectilinear [58-63] or curvilinear [72-80] coordinates; (b) the wavefunction may be expanded as a linear combination of direct product basis states [58-63] or nondirect product basis states,[64-65,81-82] based upon either harmonic oscillator single-mode functions [61,62,83] or VSCF modals [84-91] or adaptively contracted linear combinations of harmonic oscillator functions [92-93], (c) the potential energy surface may be represented: analytically, using parameterized functional forms [94-95] or; semi-analytically, using Taylor series expansions about equilibrium [96-100] or; numerically, by mapping out energies on grids.[101-102]

While different approaches to solving the nuclear vibrational problem have been investigated previously (VSCF, VPT, VCI), direct comparison has been problematic due to different methodological and algorithmic choices between methods and because each method has not been pushed to near its convergence limit.[103-105]

In this work, we apply CVPT to fourth order and VCI to its convergence limit.[106] In both cases, we employ the Watson Hamiltonian and expand the wavefunction in a direct product basis of harmonic oscillator functions.[106] This choice enables the VCI and CVPT

methods to be directly compared by holding all other algorithmic choices constant. Additional advantages include computational expedience, simplicity and ease of implementation.

The ability to accurately approximate solutions to the nuclear vibrational Schrödinger equation is a necessary but not sufficient condition for predicting observed fundamental frequencies. The other key factor is the accuracy of the underlying potential energy surface over the conformational space accessed during molecular vibrations. These considerations raise two questions: which *ab initio* electronic structure methods should be used to predict how the energy changes as a function of molecular conformation, and how should these data be collated in a useable form, *i.e.* what is the most appropriate way of mathematically representing the potential energy surface?

Full sextic force fields are formally required for CVPT4 calculations, although due to computational cost and numerical instability associated with constructing them, they are usually truncated from 6-mode to 4-mode representation (SFF-4MR) by including only terms with up to four unique indices.[107-109] Hamiltonians based upon lower order PES expansions, on the other hand, do not require full fourth-order CVPT treatment. In particular, quartic force fields are both necessary and sufficient for CVPT2 calculations.

In previous work, we have shown that SFF-4MR are required to achieve spectroscopic accuracy in VCI calculations of fundamental frequencies.[99,106] However, this procedure can be computationally intensive and scales badly with the number of vibrational modes. Truncating the PES expansion at fourth order substantially decreases the computational cost of both constructing the PES and solving the nuclear vibrational Schrodinger equation but incurs a concomitant decrease in accuracy. Although the orders of the wavefunction and PES expansions are not coupled in principle, in practice it makes sense to balance the accuracy of the nuclear vibrational structure model against the accuracy of the underlying PES; *i.e.* use higher order wavefunction expansions with higher order PES expansions.

Finally, it remains to determine the appropriate level of *ab initio* electronic structure theory to use in constructing each force field. Exact analytical Hessians are required to ensure numerical stability of the differentiation procedure used to obtain the requisite force constants, thereby precluding most density functional methods.[110] Computational efficiency is the other key constraint, as a large number of Hessian calculations are required during the numerical differentiation process. Fortunately, it has been shown that anharmonic force constants are relatively insensitive to the electronic structure model.[111] This finding motivates the use of “hybrid” force fields, in which the full anharmonic force field is generated at a modest level of theory, and empirically improved by replacing the harmonic force constants by values obtained at a higher level of theory.[112,113] Previous studies have shown that spectroscopic accuracy can only be achieved if this higher level of theory is at least CCSD(T) with a near-complete atomic orbital basis set.[114]

Finally, it must be noted that there are a range of higher order terms in the electronic Hamiltonian that are typically neglected in most electronic structure calculations, including relativistic effects, non-Born-Oppenheimer effects, and terms that depend explicitly on the inter-electronic distance. These terms are omitted because they are computationally expensive to compute and tend to only have small effects on computed properties for most common molecules near their equilibrium geometries. However, a recent benchmark study on the water molecule has shown that relativistic and non-adiabatic corrections typically contribute $< 1 \text{ cm}^{-1}$ to predicted fundamentals,[115] while R12/F12 corrections ameliorate basis set incompleteness and can contribute up to 5 cm^{-1} (QZ basis) or 2 cm^{-1} (5Z basis).[114] We acknowledge that relativistic and non-adiabatic corrections are not accounted for in the present work, and basis set incompleteness errors are only estimated.

With this exception, we are now well-positioned to explore systematically the influence of different nuclear vibrational models, potential energy surface expansions, and

levels of *ab initio* electronic structure theory on the computed fundamental frequencies of halomethanes. We will also benchmark the computed fundamentals against available high-resolution experimental data. All theory development and computation is performed in atomic units, but all results are reported in units of cm^{-1} .

2. Theory

2.1 General formalism

The Watson vibrational Hamiltonian, including Coriolis rotational coupling terms, reads:

$$\hat{H} = \hat{H}_{vib} + \hat{H}_{Cor} \quad (2.1)$$

$$\hat{H}_{vib} = -\frac{1}{2} \sum_{i=1}^M \frac{\partial^2}{\partial Q_i^2} + V(Q_1, \dots, Q_M) \quad (2.2)$$

$$\hat{H}_{Cor} = -\sum B_\alpha \sum \sum \xi_{ij}^\alpha \xi_{kl}^\alpha \left(Q_i \frac{\partial}{\partial Q_j} - Q_j \frac{\partial}{\partial Q_i} \right) \left(Q_k \frac{\partial}{\partial Q_l} - Q_l \frac{\partial}{\partial Q_k} \right) \quad (2.3)$$

where the rectilinear normal coordinates, Q_i , are defined as the linear combinations of Cartesian atomic displacements that diagonalize the Hessian in mass-weighted Cartesian coordinates. The equilibrium rotational constants, B_α , correspond to the eigenvalues of the molecular inertia tensor, and the rovibrational Coriolis coupling terms are calculated using the method of Meal and Polo.[\[116,117\]](#) The potential energy surface is expanded as a Taylor series in rectilinear normal coordinates:

$$V = \frac{1}{2} \sum_i \omega_i Q_i^2 + \frac{1}{3!} \sum_{ijk} F_{ijk} Q_i Q_j Q_k + \frac{1}{4!} \sum_{ijkl} F_{ijkl} Q_i Q_j Q_k Q_l + \dots \quad (2.4)$$

where the summation indices run from 1 through to the number of vibrational modes, M . The force constants, F_{ijkl} , are the derivatives of the potential energy with respect to the normal coordinates. The minimum energy point, first order force constants and off-diagonal second order force constants are all zero by definition.

The Hamiltonian may be re-factored into a zeroth-order, analytically solvable term, and a smaller correction term, which itself may be expanded order-by-order:

$$\hat{H} = \hat{H}_0 + \hat{H}_{pert}, \quad (2.5)$$

$$\hat{H}_0 = \hat{T}_0 + \hat{V}_0 = \frac{1}{2} \sum_{i=1}^M \left(-\frac{\partial^2}{\partial Q_i^2} + \omega_i Q_i^2 \right), \quad (2.6)$$

$$\begin{aligned} \hat{H}_{pert} &= \left(\frac{1}{3!} \sum_{ijk} F_{ijk} Q_i Q_j Q_k \right) + \left(\hat{H}_{Cor} + \frac{1}{4!} \sum_{ijkl} F_{ijkl} Q_i Q_j Q_k Q_l \right) + \dots = \\ &= \hat{V}_1 + (\hat{T}_2 + \hat{V}_2) = \hat{H}_1 + \hat{H}_2 \end{aligned} \quad (2.7)$$

2.2 VCI

In the VCI model, the nuclear vibrational wavefunction is expanded in a basis of harmonic oscillator product functions, $\Phi_{\bar{n}}$, referred to as basis states:

$$\Phi_{\bar{n}}(Q_1, \dots, Q_M) = \prod_{i=1}^M \phi_{n_i}(Q_i), \quad (2.8)$$

where \bar{n} is a string of quantum numbers, n_1, \dots, n_M , specifying the vibrational state across all M modes. The constituent harmonic oscillator functions, ϕ_{n_i} , are mode-specific analytic solutions to the zeroth-order harmonic oscillator Hamiltonian. VCI basis states are generated by specifying a maximum value for the sum of vibrational quantum numbers, N_{\max} :

$$\sum_{i=1}^M n_i = N_{\max} \quad (2.9)$$

Within the VCI context, this index is referred to as the excitation level and denoted using round bracket notation, $\text{VCI}(N_{\max})$.

The VCI wavefunction is then formed as a linear combination of basis states:

$$\Psi_{\bar{n}}(Q_1, \dots, Q_M) = \sum_{n'} c_{n, n'} \Phi_{n'}(Q_1, \dots, Q_M). \quad (2.10)$$

The coefficients are determined by forming and diagonalizing the VCI matrix, comprised of the following matrix elements, for all unique combinations of basis states:

$$\langle \Phi_n(Q_1, \dots, Q_M) | \hat{H} | \Phi_{n'}(Q_1, \dots, Q_M) \rangle. \quad (2.11)$$

The formulae required to evaluate these matrix elements are detailed in the Supporting Information.

2.3 CVPT

Details of the derivation and implementation of canonical van Vleck perturbation theory (CVPT) are scattered throughout the literature.[33,43-57] For completeness and consistency in notation, we recapitulate our approach in the Supporting Information and summarize the salient points here. Van Vleck perturbation theory is based upon finding a unitary transformation operator \hat{U} , that diagonalizes \hat{H} , preserving the eigenvalue spectrum but modifying the wavefunction,

$$\hat{H}\hat{U}\Psi = E\hat{U}\Psi \quad (2.12)$$

If \hat{H} can be fully diagonalized to \tilde{H} , via $\hat{U}^{-1}\hat{H}\hat{U} = \tilde{H}$, then the matrix eigenvalue problem becomes trivial to solve. Unfortunately, in practice, there is no direct practical way of obtaining \hat{U} for an arbitrary choice of \hat{H} . However, if the anharmonic part of \hat{H} is expanded as a *finite* power series in rectilinear normal mode coordinates, Q , CVPT provides a well-defined procedure for constructing reduced-rank approximations to \hat{U} :

$$\hat{U} \approx \prod_{k=0}^K \hat{U}_k \quad (2.13)$$

where each constituent transformation operator, \hat{U}_k , diagonalizes the k -th order perturbation term in the Hamiltonian. \hat{U}_0 represents the identity transformation that returns the Hamiltonian unchanged.

As proposed by van Vleck, the transformation operators \hat{U}_k are represented in complex exponential form, to ensure that they are unitary:

$$\hat{U}_k = \exp(i\hat{S}_k) \quad (2.14)$$

A perturbation parameter is then introduced into the original and diagonalized (denoted by tilde) forms of the Hamiltonian and into the Taylor series expansion of the transformation operator, identifying terms order-by-order:

$$\hat{H} = \hat{H}_0 + \lambda\hat{H}_1 + \lambda^2\hat{H}_2 + \dots, \quad (2.15)$$

$$\tilde{H} = \tilde{H}_0 + \lambda\tilde{H}_1 + \lambda^2\tilde{H}_2 + \dots, \quad (2.16)$$

$$\hat{U}_k = \exp(i\lambda^n\hat{S}_k). \quad (2.17)$$

Substituting these expressions into the reduced-rank form of the transformation relation and equating terms with like powers of λ reveals the recursive transformation formulae:[\[54,56\]](#)

$$\tilde{H}_k^{(K)} = \sum_{n=0}^{\lfloor k/K \rfloor} \frac{i^n}{n!} [\hat{S}_k,]^n \hat{H}_{k-nK}^{(K-1)}, \quad (2.18)$$

where k indexes terms in the Hamiltonian and K represents the transformation order, and $K < k$. Here $[\hat{S}_k,]^n \hat{H}$ is the shorthand notation for the nested commutator $[\hat{S}_k, [\hat{S}_k, \dots (n) \dots [\hat{S}_k, \hat{H}] \dots]]$, where \hat{S}_k occurs n times in this expression.

The quasi-diagonal form of the Hamiltonian is then constructed from its transformed components, wherein the k^{th} order term has been transformed to order k :

$$\tilde{H}^{(K)} = \sum_{k=0}^K \tilde{H}_k^{(k)} = \tilde{H}_0^{(0)} + \tilde{H}_1^{(1)} + \tilde{H}_2^{(2)} + \dots, \quad (2.19)$$

Finally, it remains to specify the transformation operators, \hat{S}_k . They are formulated to ensure that \hat{H} can be reduced to \tilde{H} , to order K , as described in the Supporting Information. Following Birss and Choi,[\[47\]](#) they are most concisely expressed in terms of vibrational

quanta creation and annihilation operators, a^+ and a , also known as raising and lowering operators:

$$\hat{S}_k = -i \sum_{(n,n')} \frac{c_{(\bar{n},\bar{n}')}^{(k-1)}}{\sum_{i=1}^M (n'_i - n_i) \omega_i} \prod_{i=1}^M (a_i^\dagger)^{n'_i} (a_i)^{n_i}, \quad (2.20)$$

where \bar{n}', \bar{n} are paired strings of integers as defined in the VCI section above, that together specify the powers of creation and annihilation operators required to generate terms in the Hamiltonian to order K . At the first transformation step ($K=1$), the coefficients $c_j^{(k-1)}$ are composed of the force constants within the potential energy expansion and pre-factors of kinetic energy terms. At later transformation steps they become complicated linear combinations of these original values.

The Hamiltonian can only be reduced to fully diagonal form if all the denominators in \hat{S}_k are non-vanishing. In general, this is not true, and resonant terms must be identified and excluded from the transformation procedure according to the value of the dimensionless prefactor for each set of creation/annihilation operators indexed by \bar{n}', \bar{n} :

$$\Xi_{\bar{n},\bar{n}'} = \frac{c_{(\bar{n},\bar{n}')}^{(k-1)}}{\sum_{i=1}^M (n'_i - n_i) \omega_i}, \quad (2.21)$$

and also the magnitude of its denominator:

$$\Delta_{\bar{n},\bar{n}'} = \sum_{i=1}^M (n'_i - n_i) \omega_i. \quad (2.22)$$

Thresholds for each of these quantities are denoted Ξ^* and Δ^* , respectively.

This formulation results in a quasi-diagonal matrix in which only the resonant terms are coupled through off-diagonal matrix elements. They are then treated variationally on a symmetry block-by-block basis to complete the diagonalization of the Hamiltonian.

3. Methods

3.1 PES construction

Force constants for each SFF-4MR were obtained at MP2/cc-pVTZ by numerical differentiation of analytic Hessians along rectilinear normal modes from the equilibrium geometry. All ab initio calculations were carried out using the Gaussian09 program package.^[118] To ensure sufficient precision in the computed Hessians, the following settings, screening and convergence thresholds were used (values are given in atomic units):

- (a) threshold for eliminating primitive basis functions from transformed contracted sets: 0,
- (b) two-electron integral screening threshold: 10^{-14} ,
- (c) SCF density matrix convergence threshold: 10^{-12} ,
- (d) coupled-perturbed Hartree-Fock (CPHF) convergence threshold: 10^{-12} ,
- (e) molecular and integral symmetry: turned off.

Details of the implementation and validation of our numerical differentiation procedure are provided as Supporting Information.

Finally, MP2/cc-pVTZ harmonic force constants were replaced by CCSD(T)/aug-cc-pVQZ equivalents.

3.2 Basis set incompleteness estimates

Basis set incompleteness errors in CCSD(T)/aug-cc-pVQZ harmonic force constants are estimated in one of two ways:

(*) by comparison against complete basis set limit extrapolated values, obtained using the two-point extrapolation formula of Helgaker et al. ^[119]:

$$V_{CBS} = \frac{4^3 V_{QZ} - 3^3 V_{TZ}}{4^3 - 3^3} \quad (3.1)$$

where $\nu_{QZ} - \nu_{TZ}$ are the harmonic frequencies obtained for CCSD(T)/cc-pVTZ and CCSD(T)/cc-pVQZ models, respectively. Diffuse functions are omitted because they lead to non-monotonic convergence of energies and energy-related properties.

(*) by computing the difference between CCSD(T)/aug-cc-pVTZ and CCSD(T)/aug-cc-pVQZ harmonic frequencies, which is expected to provide an upper bound to the basis set incompleteness error.

3.2 VCI

VCI(10) calculations were performed using full quartic and four mode-representation sextic force fields, with no restriction on the extent of mode-coupling or *a priori* screening of VCI matrix elements. However, to limit memory requirements, only matrix elements larger than 10^{-10} a.u. were stored. We have previously shown that VCI(10) calculations converge to within 0.1 cm^{-1} of the full VCI limit, on average, provided that the underlying force field does not diverge in the relevant energy range [83].

3.3 CVPT

CVPT2 is applied to second order to quasi-diagonalize Hamiltonians expanded to 4th order in the potential (QFF), including second-order kinetic Coriolis terms. Similarly, CVPT4 is applied to quasi-diagonalize Hamiltonians incorporating up to sextic terms in the potential (SFF-4MR).[56] Out of curiosity, we also performed CVPT4 calculations using a QFF to assess the effect of premature truncation of the PES, although this procedure is not generally recommended because it is expected to provide an unbalanced treatment of **even** single-mode anharmonicities.

Resonant states identified using the thresholds $\Xi^* = 0.06$, $\Delta^* = 600 \text{ cm}^{-1}$ were excluded from the transformation procedure. Blocks of untransformed near-resonant states were then diagonalized using VCI in a basis of states constructed by allowing up to 4 quanta of vibrational excitation.

3.4 Experimental Reference Data

Experimental fundamental frequencies for halomethanes (^{35}Cl isotopologues only) were extracted from spectroscopic data reported in the literature and correspond to ro-vibrational band centres (Q-branches, $J = 0$).^[1-23] The summary of existing literature data on fundamentals of the dihalomethanes is presented in [Table 1](#). The reported observations were carefully re-evaluated for uncertainties in absolute frequency calibration, rather than the uncertainties in relative peak positions that are often reported. All values derived from high-resolution infrared spectroscopy data are accurate to 0.005 cm^{-1} . Comparison against computed values does not require this level of accuracy; all frequencies will subsequently be reported to a maximum of 2 decimal places.

4. Results and Discussion

VCI and CVPT predictions of fundamental frequencies for CH_2F_2 , CH_2FCl and CH_2Cl_2 are presented in [Tables 2, 3, and 4](#), respectively, with symmetry labels in the first column, existing experimental reference data in the second column, reference VCI(10) computational results in the third column, and CVPT4 results in the fourth column. These results were obtained with the $\text{SFF}_{4\text{MR}}$ formulation of the sextic force field. In the last three columns are the results with VCI(10), CVPT4, and CVPT2 obtained with the QFF quartic force field. Before comparing these results in detail, we begin by establishing the accuracy of the benchmark VCI(10) values.

4.1. Convergence of VCI fundamentals with respect to excitation level

VCI/ $\text{SFF}_{4\text{MR}}$ and VCI/QFF fundamentals at a range of different excitation levels are reported in the Supporting Information and average deviations from VCI(10) values summarized in [Table 5](#).

Clearly, the VCI(10)/SFF-4MR reference values are well converged with respect to excitation level, with a mean absolute deviation of 0.03 cm^{-1} to VCI(9), and a maximum error of only 0.33 cm^{-1} . Their QFF counterparts are not quite as well converged, with mean and maximum differences between VCI(9) and VCI(10) of 0.07 cm^{-1} and 0.95 cm^{-1} , respectively. Nonetheless, these deviations fall within the bounds of “spectroscopic accuracy”, commonly defined as 1 cm^{-1} , and so can be considered acceptably converged for all practical intents and purposes.

4.2. Comparing CVPT4 and VCI(10) based upon 4MR sextic force fields

Comparing SFF-4MR data across [Tables 2-4](#) reveals a number of trends apparent for all three dihalomethanes. CVPT4 reproduces benchmark VCI(10) results to within 0.5 cm^{-1} for all fundamentals except the highest frequency stretching mode of each molecule. The CVPT4 values for these modes are in error by $1\text{--}2\text{ cm}^{-1}$. For low frequency modes ($< 800\text{ cm}^{-1}$), the agreement between VCI(10) and CVPT4 is particularly close, with errors less than 0.1 cm^{-1} .

Mean and maximum deviations between CVPT4/SFF-4MR and VCI(10)/SFF-4MR across all fundamentals of all three molecules are summarized in [Table 5](#), alongside VCI convergence data. From this table, we observe that CVPT4 produces results intermediate in accuracy between VCI(6) and VCI(7).

4.3. Comparing CVPT4 and VCI(10) based upon quartic force fields

Upon initial consideration, the CVPT4/QFF fundamentals do not appear to display any clear pattern of deviation from the benchmark VCI(10)/QFF values. However, upon closer inspection, the comparison is actually a sensitive indicator of how well the QFF describes each vibrational mode and its couplings to other modes. Where there is *very* close agreement between CVPT4 and VCI(10) predictions for a given mode (deviations $< 0.1\text{ cm}^{-1}$), the frequencies also do not change much if the quartic force field is extended to a four mode

representation sextic force field. For example, VCI(10)/QFF and VCI(10)/SFF-4MR results for these modes agree to within 1.1 cm^{-1} .

Similarly, there is much better agreement between QFF-based CVPT4 and VCI(10) results for difluoromethane, the least anharmonic of the molecules within our data set. Discrepancies increase as the fluorine atoms are substituted by chlorine, making the molecules progressively more anharmonic. The largest deviations occur in the high frequency stretching modes of CH_2FCl and CH_2Cl_2 .

Although it is difficult to predict *a priori* how well VCI/QFF and CVPT4/QFF results based upon quartic force fields will agree for any given vibrational mode, we note that the agreement is quite good overall; with a maximum deviation of $< 5\text{ cm}^{-1}$ in the ν_1 stretching mode of CH_2Cl_2 , and an average deviation of $< 2\text{ cm}^{-1}$ across all fundamental modes. Further, CVPT4 remains intermediate in accuracy between VCI(6) and VCI(7) even when the SFF-4MR is swapped for a QFF (Table 5).

4.4. Comparing VCI(10) results based on quartic and 4MR sextic force fields

As noted above, QFFs adequately describe the low frequency halogen-carbon-halogen bending modes and the internal H-C-H bending modes, because these modes are largely uncoupled from one another and from other fundamental vibrational modes within these molecules.

However, in the mid-range region of each spectrum ($900 - 2000\text{ cm}^{-1}$), the vibrational modes become a complicated mix of carbon-halogen stretches, external H-C-H bends and wags. The coupling between these modes is not adequately captured by quartic force fields, introducing errors of $4-10\text{ cm}^{-1}$ relative to benchmark VCI(10)/SFF-4MR results.

The high frequency region of each spectrum ($2000 - 3500\text{ cm}^{-1}$) contains symmetric and asymmetric C-H stretching modes that are again largely uncoupled to one another and other fundamental bending and stretching modes. In this case, the QFF no longer fails to

capture coupling between fundamentals, but instead must not adequately describe anharmonicity along each mode and/or higher-order resonances, *e.g.* Fermi resonances, which arise from couplings between these modes and accidentally near-degenerate combination bands. VCI(10)/QFF and VCI(10)/SFF-4MR predictions differ by 1-5 cm^{-1} for these modes.

4.5. Comparing CVPT2 with other approaches

CVPT2 fundamentals reproduce benchmark VCI(10)/SFF-4MR values to within 1 cm^{-1} for all modes except the high frequency C–H stretches where they can differ by up to 13 cm^{-1} . The accuracy of all CVPT models considered here is summarized in Table 6. CVPT2/QFF is, on the whole, more accurate than CVPT4/QFF, although with larger outliers amongst the stretching modes.

This overall high level of accuracy from CVPT2 can only be explained by mutual cancellation of higher order terms omitted from both the perturbation theory and force field expansions. This cancellation is known to be exact for the Morse oscillator,[\[120,121\]](#) a simple one-dimensional model system, but no such proof exists for coupled multi-dimensional oscillators. Nonetheless, the empirical evidence presented here is strong and is supported by comparing CVPT2 and VCI(10) results generated using the *same* quartic force field that show larger deviations, particularly in the mid-range region of the spectrum.

It is perhaps surprising that CVPT2 deviates most from VCI(10)/SFF-4MR in the high frequency C-H stretching region of the spectrum, because the region of the PES describing these modes should be well fitted using a concise series expansion in Morse oscillator coordinates. Yet, it is clear that these modes must not behave like uncoupled Morse oscillators but must display effects through strong mode-mode coupling, altered anharmonicity profiles along each mode, or both.

We have therefore investigated the underlying cause of the unusually large changes observed in some fundamental stretching mode transitions of halomethanes when upgrading

the model from CVPT2/QFF to CVPT4/SFF-4MR. By analysing the coupling strengths within blocks of accidentally near-degenerate fundamental and overtone modes, we find that the dominant cause of the discrepancy is due to changes in how well the coupling between the fundamentals and near-degenerate combination bands are modelled.

For example, the ν_6 mode of CH_2F_2 changes by -11.50 cm^{-1} going from CVPT2/QFF to CVPT4/SFF-4MR, because it is near-degenerate with the combination bands $\nu_2+\nu_7$ and $\nu_5+\nu_8$. The shift due to Fermi resonance is better modelled at CVPT4, decreasing from 61.5 cm^{-1} to 45.4 cm^{-1} (-16.1 cm^{-1}). This effect is somewhat offset by a decrease in the ν_6 single-mode anharmonicity that increases the frequency. The $\nu_2+\nu_7$ and $\nu_5+\nu_8$ combination modes are coupled via Darling-Dennison resonance, but this only affects the ν_6 frequency indirectly by influencing the extent of configurational mixing of $\nu_2+\nu_7$ and $\nu_5+\nu_8$ with ν_6 . Full details of our analysis are provided as Supporting Information.

Similarly, the ν_1 mode of CH_2FCl exhibits three Fermi resonances, this time with doubly-excited fundamentals $2\nu_2$, $2\nu_3$ and $2\nu_8$, whose couplings are more accurately captured at CVPT4. This results in the fundamental frequency decreasing by 11.34 cm^{-1} .

The ν_1 mode of CH_2Cl_2 also couples with its doubly-excited fundamentals $2\nu_2$ and $2\nu_8$, and the frequency drops by 7.5 cm^{-1} going from CVPT2/QFF to CVPT4/SFF-4MR. We note that this direction of change is not universal; CVPT4/SFF-4MR fundamental frequencies can also be higher than their CVPT2/QFF counterparts.

4.6. Comparing theory with experiment

Both the CVPT4 and VCI(10) models based upon our hybrid CCSD(T)/MP2 SFF_{4MR} PES yield fundamental frequencies within 2 cm^{-1} of experiment, on average, with maximum deviations $< 5 \text{ cm}^{-1}$, except for the $\nu_5(\text{A}_2)$ mode of CH_2Cl_2 whose computed frequency of 1163 cm^{-1} is 10 cm^{-1} higher than the value of 1153 cm^{-1} reported from gas-phase Raman observations by Welsh et al. [15] and quoted in a gas-phase IR study by Duncan et al. [17]

This large discrepancy led us to re-evaluate the experimental observations for the A_2 mode. Welsh and coworkers [15] interpreted the observed band shape as being similar to a B-type band in an IR spectrum. However, the selection rules for rotational transitions in the Raman effect differ from those in IR spectra; thus, such an analogy does not apply. A more likely interpretation of the Raman band shape is that it represents a fundamental on the high frequency end of the band accompanied by a hot band progression spilling to low frequency. This interpretation would make the frequency of the fundamental higher than 1153 cm^{-1} .

In response to our request, Dr. Thomas A. Blake at Pacific Northwest National Laboratory supplied a detailed gas-phase IR spectrum of CH_2Cl_2 in the 1150 cm^{-1} region.[122] That spectrum is displayed in Figure 1. It clearly shows a sharp Q-branch feature at 1158.2 cm^{-1} , which can be attributed to the A_2 mode of CH_2Cl_2 made weakly active by Coriolis coupling. The broad band at 1184 cm^{-1} is assigned to $281.5(A_1) + 898.66(B_1)$. We do not have an assignment for the band with the sharp Q branch at 1223.1 cm^{-1} . A possible explanation for the gas-phase Raman band at 1153 cm^{-1} [15] is a difference band, $1435(A_1) - 281.5(A_1) = 1153.5\text{ cm}^{-1}$.

4.7. Remaining sources of error

We have demonstrated above that the VCI(10) fundamentals are converged to well within 1 cm^{-1} with respect to the completeness of the underlying harmonic oscillator product basis, from which the VCI wavefunction is constructed, and that CVPT4 fundamentals agree with VCI(10) results to within 1.7 cm^{-1} , with a mean absolute deviation of only 0.3 cm^{-1} . Therefore, differences between computed and observed fundamentals are not primarily due to deficiencies in the wavefunction and must be due to inaccuracy and/or incompleteness in the underlying PES expansion.

We have previously shown that four mode-representation sextic force fields reproduce results from full sextic force fields to within 1 cm^{-1} [83]. It is unlikely that including higher

order terms in the PES expansion would have a large effect. This supposition is supported by previous studies that have demonstrated close agreement between experimental fundamentals and those calculated using sextic force fields.[123]

Consequently, the choice of electronic structure models used in constructing the PES is most likely the dominant remaining accuracy-determining factor. Others have shown that anharmonic force constants are relatively insensitive to the level of *ab initio* theory.[111] And, in any case, it is difficult to explore alternatives, due to the computational expense associated with calculating the required set of higher order force constants.

Therefore, we focus on estimating basis set incompleteness errors in the CCSD(T)/aug-cc-pVQZ harmonic force constant component of the potential energy surface expansions. This deficiency is expected to be the dominant source of error in the computed anharmonic frequencies, because the largest contribution to the anharmonic frequencies comes from the zeroth-order harmonic terms.

CCSD(T)/aug-cc-pVQZ harmonic frequencies are presented in Table 7, along with two different estimates of basis set incompleteness errors, as described in the methods section. Most of the estimated errors fall in the $2 - 5 \text{ cm}^{-1}$ range, comparable to the magnitude of the difference between computed VCI(10)/SFF_{4MR} fundamentals and corresponding experimental values.[124-126]

More detailed analysis reveals that the estimated basis set incompleteness errors in CCSD(T)/aug-cc-pVQZ harmonic frequencies are greater than the difference between computed anharmonic frequencies and experiment for any given vibrational mode. This finding suggests that either our error estimates are conservative, or that there is cancellation of electronic structure model errors between the harmonic and anharmonic parts of the potential, or both.

Either way, having eliminated or controlled for all dominant sources of error, we are confident that errors due to the underlying electronic structure models account for the majority of the remaining difference between computed and experimentally observed fundamental frequencies. This finding is consistent with previous computational results that show errors of around 5 cm^{-1} in anharmonic CCSD(T)/AVQZ fundamentals.[114]

4.8. Computational cost

In choosing a computational model for simulating IR spectra, the key considerations are accuracy, ease of use, and computational cost. We have thoroughly investigated the relative accuracy of VCI and CVPT models. In principle, they are both equally easy to use and can be readily adapted to calculate intensities, provided appropriate dipole moment surfaces are available, although the calculation of intensities is not addressed in the current work. It remains to consider the computational cost of each nuclear vibrational model.

In principle, the time required to compute all VCI matrix elements and the memory required to store them scales as $O(M^{2N_{\max}})$ where M is the number of vibrational modes, but this may be reduced to $O(M^6)$ by judicious use of pre-screening and applying reduced mode-coupling constraints on the VCI basis states.[83]

We have performed a preliminary investigation into the scaling of CVPT models with number of vibrational modes, using single C_{2v} -symmetric molecules of different sizes (HF, H₂O, H₂CO, CH₂F₂). From the raw data presented in the Supporting Information, we find that CVPT2 scales approximately as $O(M^{3-4})$ and CVPT4 approximately as $O(M^{4-5})$. Clearly, CVPT is a more economic choice than VCI models of equivalent accuracy. Practically, we note that operator version CVPT2 has been applied to molecules with up to 12 atoms,[127-128] VCI to molecules with up to 10 atoms,[83] and CVPT4 to molecules with up to 8 atoms.[56]

5. Conclusions

One of the major challenges in simulating anharmonic vibrational spectra is obtaining an appropriately accurate representation of the potential energy surface in a form that facilitates solving the nuclear vibrational Schrödinger equation. If this barrier can be overcome, e.g. by constructing ‘hybrid’ sextic four mode-representation force fields at the MP2/cc-pVTZ level and replacing the harmonic force constants with CCSD(T)/aug-cc-pVQZ equivalents, then both VCI(6) and CVPT4 are suitable methods for obtaining approximate solutions to the the nuclear vibrational Schrödinger equation. They are of comparable accuracy to one another, and both introduce errors far smaller ($1-2\text{ cm}^{-1}$) than those inherent in the underpinning electronic structure models ($\sim 5\text{ cm}^{-1}$). However, should only a quartic force field be available, then CVPT2 often outperforms more sophisticated VCI models, due to fortuitous error cancellation that arises from simultaneously truncating both the perturbation theory and potential energy surface expansions.

Table 1. Ro-vibrational band centres for fundamental vibrational transitions in dihalomethanes.

CH ₂ F ₂			CH ₂ F ³⁵ Cl			CH ₂ ³⁵ Cl ₂		
ν (cm ⁻¹)	\pm (cm ⁻¹)	Ref	ν (cm ⁻¹)	\pm (cm ⁻¹)	Ref	ν (cm ⁻¹)	\pm (cm ⁻¹)	Ref
528.7044	0.0006	[1]	385 ^b	1	[12]	281.5 ^c	1.5	[16]
1090.1264	0.0002	[8]	761.4403	0.0004	[13]	717.4675	0.0005	[21]
1111.5162	0.0002	[8]	1002.3349	0.0004	[11]	759.8486	0.0005	[21]
1178.6414	0.0002	[8]	1067.7991	0.0004	[14]	898.6648	0.005	[18]
1255.8285	0.0002	[8]	1236.8219	0.0010	[10]	1153 ^d	1.5	[16]
1435.6357	0.0002	[6]	1353.3173	0.0008	[9]	1268.8514	0.0005	[22]
1509.1492	0.0002	[6]	1473.6	0.5	[12]	1435.0	0.2	[17]
2947.9 ^a	> 1	[7]	2992.57	0.1	[12]	2997.7	0.2	[17]
3014.0503	0.0003	[4]	3035.38	0.1	[12]	3055	1.5	[16]

^a An uncertain assignment, based on a Q-branch feature that should be B-type and have no central Q branch. The uncertainty could be several cm⁻¹.

^b A weak Q branch at ~ 385 cm⁻¹ is probably the best estimate of the centre frequency for this band.

^c Mutual observations of frequencies from IR and Raman spectra suggest that the Raman observations below 2000 cm⁻¹ are 1 cm⁻¹ too low. Thus, a correction has been applied.

^d Assignment uncertain, will be revisited in the present work.

Table 2. Computed and experimental fundamental frequencies of CH₂F₂, according to VCI and CVPT models using quartic (QFF) and 4 mode-representation sextic (SFF-4MR) force fields. All quantities reported in cm⁻¹. Δ represents the signed deviation of the CVPT4/SFF-4MR values from the benchmark VCI(10)/SFF-4MR data.

Experimental			SFF-4MR			QFF		
Label	Sym	Freq	VCI(10)	CVPT4	Δ	VCI(10)	CVPT4	CVPT2
v ₄	A ₁	528.70	526.43	526.40	-0.03	526.35	526.34	526.42
v ₉	B ₂	1090.13	1088.46	1088.37	-0.09	1089.93	1089.78	1087.84
v ₃	A ₁	1111.52	1108.53	1108.53	-0.00	1109.65	1109.58	1108.36
v ₇	B ₁	1178.64	1177.34	1177.22	-0.12	1173.21	1173.78	1177.44
v ₅	A ₂	1255.83	1255.33	1255.22	-0.11	1250.54	1251.26	1255.38
v ₈	B ₂	1435.64	1432.63	1432.57	-0.06	1428.01	1428.70	1432.82
v ₂	A ₁	1509.15	1508.95	1508.89	-0.06	1504.57	1505.23	1509.64
v ₁	A ₁	2947.9	2948.33	2948.32	-0.01	2949.33	2949.07	2952.07
v ₆	B ₁	3014.05	3010.75	3011.95	+1.20	3015.42	3015.19	3023.45

Table 3. Computed and experimental fundamental frequencies of $\text{CH}_2\text{F}^{35}\text{Cl}$, according to VCI and CVPT models using quartic (QFF) and 4 mode-representation sextic (SFF-4MR) force fields. All quantities reported in cm^{-1} . Δ represents the signed deviation of the CVPT4/SFF-4MR values from the benchmark VCI(10)/SFF-4MR data.

Experimental			SFF-4MR			QFF		
Label	Sym	Freq	VCI(10)	CVPT4	Δ	VCI(10)	CVPT4	CVPT2
ν_6	A'	383.5	382.76	382.69	-0.07	382.63	382.64	382.75
ν_5	A'	761.44	757.26	757.19	-0.07	757.47	757.47	757.21
ν_9	A''	1002.33	1002.99	1002.67	-0.32	995.99	997.22	1002.99
ν_4	A'	1067.80	1066.89	1066.86	-0.03	1067.90	1067.88	1066.32
ν_8	A''	1236.82	1235.77	1235.64	-0.13	1230.12	1231.10	1235.71
ν_3	A'	1353.32	1350.71	1350.33	-0.38	1344.37	1345.47	1350.77
ν_2	A'	1473.6	1475.94	1475.76	-0.18	1470.25	1471.24	1476.27
ν_1	A'	2992.57	2996.38	2995.97	-0.41	2992.87	2995.51	3007.32
ν_7	A''	3035.38	3033.96	3035.34	+1.38	3037.46	3039.14	3039.58

Table 4. Computed and experimental fundamental frequencies of $\text{CH}_2^{35}\text{Cl}_2$, according to VCI and CVPT models using quartic (QFF) and 4 mode-representation sextic (SFF-4MR) force fields. All quantities reported in cm^{-1} . Δ represents the signed deviation of the CVPT4/SFF-4MR values from the benchmark VCI(10)/SFF-4MR data.

Experimental			SFF-4MR			QFF		
Label	Sym	Expt	VCI(10)	CVPT4	Δ	VCI(10)	CVPT4	CVPT2
ν_4	A ₁	281.5	281.32	281.32	0	281.23	281.24	281.32
ν_3	A ₁	717.47	715.27	715.27	0	715.41	715.48	715.27
ν_9	B ₂	759.85	759.54	759.63	+0.09	759.83	759.91	759.38
ν_7	B ₁	898.66	899.11	898.73	-0.38	888.91	891.01	899.00
ν_5	A ₂	1158.2	1163.28	1163.09	-0.19	1155.41	1157.00	1163.36
ν_8	B ₂	1268.85	1270.54	1270.32	-0.22	1262.87	1264.47	1271.10
ν_2	A ₁	1435	1437.93	1437.58	-0.35	1430.03	1431.67	1437.94
ν_1	A ₁	2997.7	3001.06	3001.34	+0.28	2999.25	3003.79	3008.85
ν_6	B ₁	3055	3057.62	3058.93	+1.31	3062.84	3064.29	3058.31

Table 5. Mean absolute and maximum deviations of $VCI(n)$ ($5 < n < 10$) and CVPT4 fundamentals from $VCI(10)$ reference data, across all modes of all 3 molecules. The force fields used with each method are given in the top row. All quantities reported in cm^{-1} .

n	SFF-4MR		QFF	
	MAD	MAX	MAD	MAX
9	0.03	0.33	0.07	0.95
8	0.09	0.81	0.16	2.08
7	0.24	0.85	0.47	3.59
6	0.69	2.19	1.12	5.90
5	1.08	3.92	1.64	9.17
CVPT4	0.29	1.68	0.93	4.54

Table 6. Mean absolute and maximum deviations of CVPT2/QFF, CVPT4/QFF and CVPT4/SFF-4MR fundamentals from $VCI(10)$ /SFF-4MR reference data, across all modes of all 3 molecules. All quantities reported in cm^{-1} .

	MAD	MAX
CVPT4/SFF-4MR	0.29	1.38
CVPT4/QFF	3.24	8.23
CVPT2/QFF	1.67	12.63

Table 7. CCSD(T)/aug-cc-pVQZ fundamental frequencies (ν) and associated error estimates:

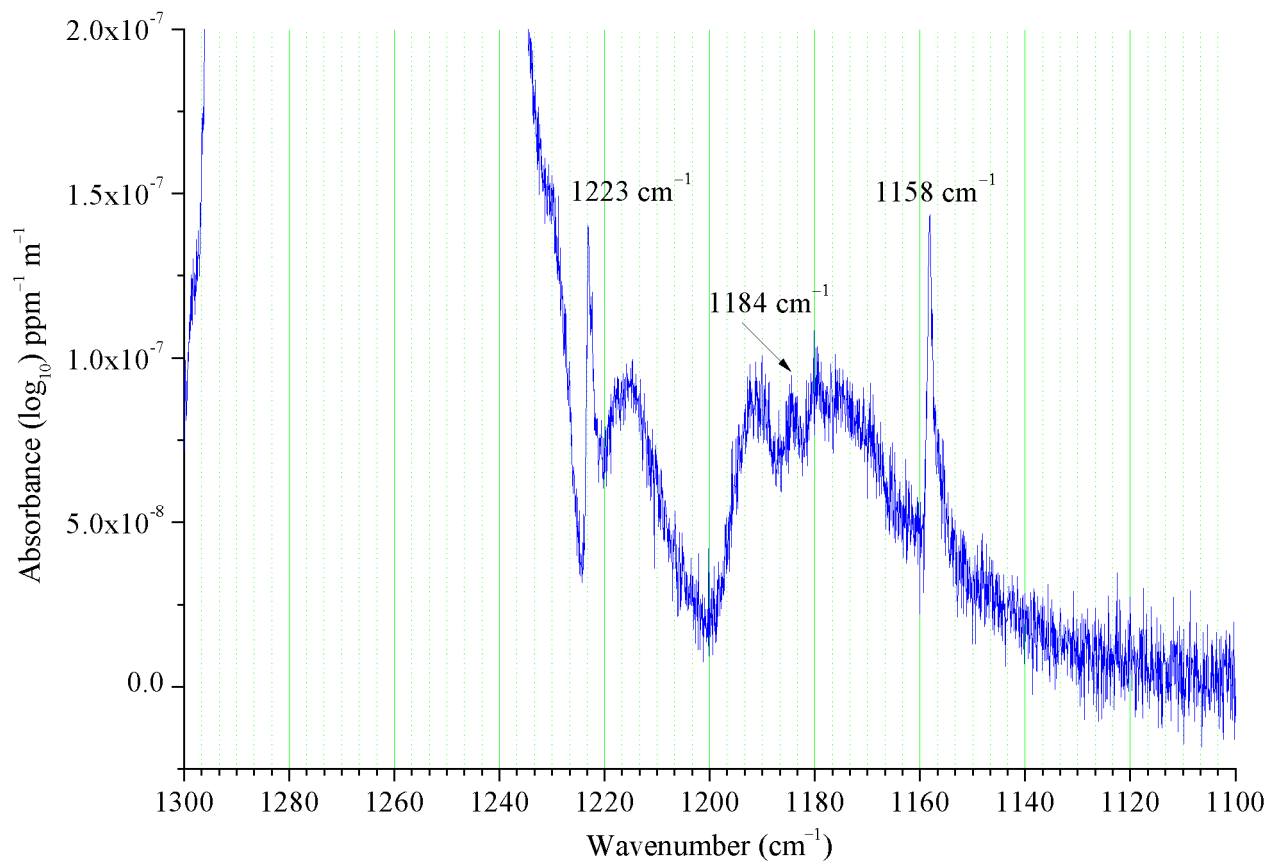
$$\Delta_{\text{CBS}} = \text{CCSD(T)/CBS}_{\text{extrap}} - \text{CCSD(T)/aug-cc-pVQZ},$$

$$\Delta_{\text{aTZ}} = \text{CCSD(T)/aug-cc-pVQZ} - \text{CCSD(T)/aug-cc-pVTZ}$$

All quantities reported in cm^{-1} .

CH ₂ F ₂			CH ₂ FCl			CH ₂ Cl ₂		
ν	$ \Delta_{\text{CBS}} $	$ \Delta_{\text{aTZ}} $	ν	$ \Delta_{\text{CBS}} $	$ \Delta_{\text{aTZ}} $	ν	$ \Delta_{\text{CBS}} $	$ \Delta_{\text{aTZ}} $
533.09	2.54	3.44	387.16	2.28	2.00	284.84	0.99	0.50
1116.96	0.85	4.82	773.80	5.05	6.19	727.70	4.80	5.66
1131.40	2.19	3.39	1018.38	4.00	0.28	779.82	5.33	8.61
1197.72	3.79	5.45	1095.09	0.56	3.91	911.26	0.30	2.21
1288.28	1.95	8.56	1266.75	2.79	5.58	1188.78	2.32	0.91
1467.76	3.01	1.48	1381.31	4.73	2.72	1295.88	2.06	4.10
1550.07	1.69	2.73	1516.52	0.79	2.33	1477.64	2.32	5.95
3079.96	5.87	3.32	3104.41	3.52	2.18	3126.78	1.20	0.05
3155.39	4.97	4.84	3182.51	3.96	3.92	3205.97	2.76	3.24

Figure 1. Dichloromethane IR absorption spectrum in the range 1200-1100 cm^{-1} . Conditions: 25°C, 0.1 cm^{-1} instrument resolution, composite spectrum, sample pressure raised to 1 atm with nitrogen.



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