Geometric Energy Derivatives at the Complete Basis Set Limit: Application to the Equilibrium Structure and Molecular Force Field of Formaldehyde

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Abstract

Geometric energy derivatives which rely on core-corrected focal-point energies extrapolated to the complete basis set (CBS) limit of coupled cluster theory with iterative and noniterative quadruple excitations, CCSDTQ and CCSDT(Q), are used as elements of molecular gradients and, in the case of CCSDT(Q), expansion coefficients of an anharmonic force field. These gradients are used to determine the CCSDTQ/CBS and CCSDT(Q)/CBS equilibrium structure of the S_0 ground state of H_2CO where excellent agreement is observed with previous work and experimentally derived results. A fourth-order expansion about this CCSDT(Q)/CBS reference geometry using the same level of theory produces an exceptional level of agreement to spectroscopically observed vibrational band origins (VBOs) with a MAE of 0.57 cm^{-1}. Second-order vibrational perturbation theory (VPT2) and variational discrete variable representation (DVR) results are contrasted and discussed. Vibration-rotation, anharmonicity, and centrifugal distortion constants from the VPT2 analysis are reported and compared to previous work. Additionally, an initial application of a sum-over-states fourth-order vibrational perturbation theory (VPT4) formalism is employed herein, utilizing quintic and sextic derivatives obtained with a recursive algorithmic approach for response theory.

1 INTRODUCTION

Spectroscopic accuracy, where deviations from gas-phase vibrational band origins (VBO's) does not exceed 1 cm^{-1}, has been a longstanding goal of theoretical spectroscopy.[1] Empirically fit[2–5] potential energy surfaces (PESs) are capable of providing spectroscopic accuracy for a system if a very high-quality *ab initio* PES is available and hundreds of rotationally resolved spectroscopic observations about well-defined VBOs have been for reported for that system. Such empirical reliance obsfucates the powerful predictive ability of theory which most often seeks to describe the properties of systems that are difficult to study in the laboratory. High-accuracy benchmark work[6–8] on the rovibrational spectrum of water shows that *ab initio* PESs alone are capable of spectroscopic accuracy for VBOs as long as complete basis set (CBS) extrapolations and extensive correlation energy corrections are utilized. Quantum chemistry has reached a point where fully *ab initio* PESs of this quality are now available for several small molecules[9–13] but the cost associated with higher-order correlation corrections has prevented their development as a routine practice.

The effectiveness of composite approaches to the total energy of a system is emphasized in the current work through the use of a focal-point analysis (FPA)[14–17] that provides a spectroscopically accurate PES through high-level, size-extensive coupled cluster computations. Recent advances involving a (spin-free) orbital representation of the cluster amplitudes combined with a spin summation technique have made otherwise prohibitive coupled cluster models tractable.[18] These models of correlation include the coupled cluster singles, doubles, iterative triples (CCSDT), noniterative quadruples (CCSDT(Q)), and iterative quadruples (CCSDTQ) methods. The benefits of including the complete $\hat{T}_3$ and $\hat{T}_4$ excitation operators[19–22] have been known for some time, but the noniterative quadruple-excitation model[23] is comparatively new. Due to its relative cost and exemplary performance, CCSDT(Q) has been suggested as the "platinum standard" of quantum chemistry for high-accuracy studies.[24] All of these high-level correlation methods have been shown to converge faster through sub- and micro-iterations, which further increases their applicability by decreasing the time to solution.[25]

The progress made in high-level coupled cluster methods is leveraged in this work by determining the equilibrium geometry and fundamental VBOs of the ground state of formaldehyde (S_0 H_2CO), using geometric energy derivatives determined numerically from focal-point energies. Formaldehyde benefits from decades of research using high-resolution gas-phase spectroscopy to describe the vibrational[26–29] and rotational[30,31] (as well as rovibrational in databases such as HITRAN2016[32]) characteristics of the parent molecule and its isotopologues.[33] Multiple empirically refined PESs[2–5] for S_0 H_2CO have been generated over the years which form an excellent basis of comparison to the current high-accuracy *ab initio* work. The ground-state equilibrium structure (r_e) of formaldehyde has been previously optimized at the CBS limit with high-level correlation energy corrections[34] but the effects of high-level corrections on molecular vibrations and higher-order spectroscopic constants have not been evaluated. The reason for this shortcoming is obvious: the computational cost of quadruple-excitation coupled cluster models has discouraged their use in the development of anharmonic force fields until now.

Molecular force fields of small polyatomic systems have been produced through quartic using CBS-extrapolated composite energies in the past,[35–39] but only benchmark computations on triatomic systems[9] have incorporated quadruple excitation contributions to the correlation energy. A quartic force field (QFF) for S_0 formaldehyde using correlated methods up to CCSDT(Q) and basis sets as large as cc-pV6Z is presented here. QFFs provide a tractable alternative to full-dimensional PESs, which can require 50-100 times the number of displaced nuclear configurations as a QFF, when only the near-equilibrium properties of a molecule, such as fundamental vibrational frequencies, are desired. Such tractability allows for the high-throughput production of accurate spectroscopic data that is critical in the detection and characterization of molecules, especially for larger systems.

Second-order vibrational perturbation theory (VPT2) is used in this work to provide higher-order spectroscopic constants and vibrational frequencies for S_0 H_2CO and compared to a discrete variable representation (DVR) variational approach. The convergence of the VPT2 fundamental frequencies of S_0 formaldehyde to the new CCSDT(Q)/CBS standard is examined using a series of lower level CCSD(T)/cc-pVXZ (X=T,Q,5) QFFs. Additionally, an initial application of vibrational perturbation theory to fourth order (VPT4) is presented, which relies on fifth- and sixth-order geometric energy derivatives provided by a recursive and generalorder implementation of response theory.[40] A high-accuracy Morse-based PES generated here is used to fit another, complimentary, dimensionless coordinate PES for use with VPT4. Together, the two datasets offer a basis of comparison for follow-on studies in nuclear motion theory.

2 THEORETICAL METHODS

2.1 Complete Basis Set Extrapolation

All CBS extrapolation formulae assume the use of a hierarchy of basis sets that contain an increasing number of one-electron basis functions. As basis set size increases, an exact description of the Hartree-Fock electron density should be approached and diverse sets of virtual orbitals should be provided for the description of electron correlation. The correlation-consistent, polarized-valence, family of basis sets (cc-pVXZ, aug-cc-pVXZ, cc-pCVXZ, cc-pwCVXZ; X=D, T, Q, 5, 6)[41–43] were designed to have these properties. The Hartree-Fock energy extrapolation formula of Feller[44] as well as that of Helgaker et al. for the correlation energy[45] were developed using the correlation-consistent family of basis sets. The three-parameter exponential fit,[44]

$$E_X^{\mathrm{HF}} = E_\infty^{\mathrm{HF}} + ae^{-bX}, \tag{1}$$

relies on a system of direct-fit or least-squares equations involving Hartree-Fock energies computed using at least three correlation-consistent basis sets. The slower convergence[46–48] of the correlation energy (regardless of ansatz used) relative to the Hartree-Fock energy prompted Helgaker et al. to develop a separate two-parameter fit[45] of the correlation energy,

$$E_X^{\mathrm{total}} - E_X^{\mathrm{HF}} = \varepsilon_\infty^{\mathrm{corr}} + aX^{-3}, \tag{2}$$

where X is the cardinality of the correlation consistent basis set, noting that a sequence of basis sets is required to solve for extrapolated energies. The extrapolation formulae used above are just two of the many approaches available in the literature for CBS energy extrapolations.[49] Other popular methods for the extrapolation of energies include the three-point scheme of Martin and Lee[50] as well as numerous formulations from Schwenke.[51]

2.2 The Focal-Point Approach

Focal point analysis (FPA) is a dual-extrapolation composite energy scheme that systematically approaches the full configuration interaction (FCI) complete basis set (CBS) limit. The one-particle basis set limit is targeted in both the reference (Hartree-Fock) energy as well as the correlation energy. In this way, errors associated with the basis set dependence of the CCSD(T) energy is minimized. The unrecovered correlation energy is primarily accounted for by more complete models of n-particle excitation. These high level contributions to the correlation energy are represented in FPA as energy increments and appear as high level corrections (E_{hlc}) in model chemistries such as HEAT.[52–54] Energy increments are defined as the difference in the correlation energy using two separate but "adjacent" methods in the coupled cluster (or Møller-Plesset) hierarchy which rely on the same one-particle basis set.

The correlation hierarchy of methods used in FPA, such as the HF→MP2→CCSD→ CCSD(T)→CCSDT→CCSDT(Q) hierarchy used here, is used to determine method adjacency and is almost always reported explicitly or in the form of a FPA table such as the example in Table 1. A common example of an energy increment is the one associated with the correlation energy recovered using the iterative triple excitations model of coupled cluster theory: $\delta E_X^{\text{T}} = E_X^{\text{CCSDT}} - E_X^{\text{CCSD(T)}}$. The defining n-particle excitation model is used as the energy increment superscript to convey that the correlation energy being recovered by the additive difference term is, in this example, from the iterative triples (CCSDT) results using a cc-pVXZ basis set. These increments rely solely on the correlation energy components of the methods employed, since the reference energy cancels when using the same one-particle basis set.

The core-corrected focal-point energy used in this study is defined by five components; four of which define the FPA energy and one which corresponds to the core correction. In the equation below, E is an absolute energy and ΔE is the difference between two absolute energies.

$$
\begin{aligned}
E_{\mathrm{CBS}}^{\mathrm{CCSDT(Q)}} &= \left(E_6^{\mathrm{HF}} - \frac{\left(E_6^{\mathrm{HF}} - E_5^{\mathrm{HF}}\right)^2}{E_6^{\mathrm{HF}} - 2E_5^{\mathrm{HF}} + E_4^{\mathrm{HF}}} \right) + \left(\varepsilon_6^{\mathrm{(T)}} - \frac{\varepsilon_6^{\mathrm{(T)}} - \varepsilon_5^{\mathrm{(T)}}}{1 - \left(\frac{6}{5}\right)^3} \right) \\
&\quad + \left(E_4^{\mathrm{T}} - E_4^{\mathrm{(T)}} \right) + \left(E_3^{\mathrm{(Q)}} - E_3^{\mathrm{T}} \right) + \left(E_{4,\mathrm{ae}}^{\mathrm{(T)}} - E_{4,\mathrm{fc}}^{\mathrm{(T)}} \right) \\
&= E_\infty^{\mathrm{HF}} + \varepsilon_\infty^{\mathrm{(T)}} + \delta E_4^{\mathrm{T}} + \delta E_3^{\mathrm{(Q)}} + \Delta E_{\mathrm{core}} \qquad (3)
\end{aligned}
$$

Any term represented by ε_X^n is the correlation energy of a given method defined as $E_X^n - E_X^{HF}$ where n represents the defining excitation term of the model such as (T) in CCSD(T). Energy increments described as δE^n or $\delta \varepsilon^n$ are equivalent. The final term in this energy is the core correlation correction which relies on the cc-pCVXZ basis set.[43] It is defined as the difference between the CCSD(T) energy with all electrons correlated and the energy within the frozen core approximation. Two energy increments are used in the present work, δE_4^{T} and $\delta E_3^{\mathrm{(Q)}}$, to define the CCSDT(Q)/CBS focal-point energy as seen in Equation 3.

2.3 Equilibrium Structure Optimization

Molecular structures are optimized with numerical gradients determined through three-point or five-point central finite difference formulae using the findiff module of PSI4.[55] The C_{2v} ground state structure of formaldehyde requires 6 or 12 displaced geometries per numerical gradient. CCSDT(Q)/CBS core-corrected focal-point energies are computed at each displaced geometry required for calculation of the three and five-point gradient. The efficacy of core corrections in composite approaches is evaluated through comparison of the three-point CCSDT(Q)/CBS geometry to a three-point optimized ae-CCSDT(Q)/CBS structure. Additionally, a CCSDTQ/CBS geometry, which relies on iterative CCSDT/cc-pV5Z and CCSDTQ/cc-pVTZ additive corrections, is determined using five-point gradients. The

CCSDTQ/CBS level of theory is shown below in the aforementioned notation.

$$E_{\text{CBS}}^{\text{CCSDTQ}} = E_{\infty}^{\text{HF}} + \varepsilon_{\infty}^{(\text{T})} + \delta E_{5}^{\text{T}} + \delta E_{3}^{\text{Q}} + \Delta E_{\text{core}} \tag{4}$$

Relativistic corrections, Δ_{rel}, are determined as the difference between the simple internal coordinates of structures optimized at ae-CCSD(T)/cc-pCVQZ corrected with mass-velocity as well as one- and two-electron Darwin terms (MVD2)[56,57] and ae-CCSD(T)/cc-pCVQZ (referred to below as nonrel).

$$r_{\text{CBS}+\Delta_{\text{rel}}} = r_{\text{CBS}} + (r_{\text{MVD2}} - r_{\text{nonrel}}) \tag{5}$$

The r coordinate shown in Eqn. 5 is representative of any corrected simple internal coordinate; angle or bond distance. A root-mean-square (RMS) force convergence threshold of 1×10^{-7} E_h/a_0 is used for all CBS structures. Analytic gradients implemented in CFOUR 2.0 are used to optimize the reference structures for the CCSD(T)/cc-pVXZ (X=T,Q,5) levels of theory and are converged with a force RMS threshold of 1×10^{-9} E_h/a_0.[58]

2.4 CBS Extrapolation of Analytic Gradients

Although the numerical gradients used here benefit from an clearly parallelized computational strategy, analytic gradients will always be preferred when available as they are much faster to compute, are independent of system size, and suffer much less from numerical errors.[59,60] A brief derivation of how common CBS formulae may be extended to include first-order geometric derivatives is presented below. Solution of the a, b, c coefficients in an exponential fit[44] produces an easily implemented form of the CBS extrapolation of Hartree-Fock energies by way of:

$$E_{\infty} = E_3 - \frac{(E_3 - E_2)^2}{E_3 - 2E_2 + E_1} = E_3 - \frac{A^2}{B}. \tag{6}$$

In the above form, Hartree-Fock energies computed using correlation-consistent basis sets are presented as E_n where the highest n corresponds to the largest basis set used. Differentiation of the extrapolation formula with respect to a generic variable x representing a nuclear coordinate in the Cartesian frame provides a direct method of extrapolation of analytic gradients to the complete one-particle basis set limit:

$$\frac{\partial E_\infty}{\partial x} = (1 - 2AB^{-1} + A^2B^{-2})\,\frac{\partial E_3}{\partial x} + 2(AB^{-1} - A^2B^{-2})\,\frac{\partial E_2}{\partial x} + A^2B^{-2}\,\frac{\partial E_1}{\partial x} \tag{7}$$

The same principles used for the above derivation can be applied to Helgaker et al.'s extrapolation formulae for the correlation energy.[45]

$$E_\infty = E_2 - \frac{E_2 - E_1}{1 - (X_2/X_1)^3} = E_2 - Ac^{-1} \tag{8}$$

$$\frac{\partial E_\infty}{\partial x} = (1 - c^{-1})\frac{\partial E_2}{\partial x} + c^{-1}\frac{\partial E_1}{\partial x} \tag{9}$$

The denominator shown above is a simple constant term represented as c, whereas the electronic energies that enter the extrapolation are described by the difference term A. In both the reference and correlated results, the A and B variables are linear with respect to the electronic energies and the $\partial E_n/\partial x$ terms are independent of one another. The formulae derived above are with respect to a general variable x where x is chosen to be a geometric variable in this study. Similar approaches have been employed in past studies[34,61,62] with great success. However, the extrapolation of other types of energy derivatives may be better suited to a parameterized extrapolation, such as those in Ref. 63, as suggested by recent work on hyperpolarizabilities.[64]

2.5 Quartic Force Fields

A local expansion of the CCSDT(Q)/CBS potential with respect to a set of curvilinear internal coordinates is produced to fourth order about the five-point CCSDT(Q)/CBS optimized geometry. The set of coordinates chosen are redundant simple internal coordinates of formaldehyde: r_{CO}, r_{CH}, r'_{CH}, θ_{OCH}, θ'_{OCH}, τ_{HCOH}. Symmetry-adapted internal coordinates are formed following the set described by Martin et al.:[65]

$$\begin{aligned}
S_1(a_1) &= \frac{1}{\sqrt{2}}(r_{\text{CH}} + r'_{\text{CH}}) \\
S_2(a_1) &= r_{\text{CO}} \\
S_3(a_1) &= \frac{1}{\sqrt{2}}(\theta_{\text{OCH}} + \theta'_{\text{OCH}}) \\
S_4(b_1) &= \tau_{\text{HCOH}} \\
S_5(b_2) &= \frac{1}{\sqrt{2}}(r_{\text{CH}} - r'_{\text{CH}}) \\
S_6(b_2) &= \frac{1}{\sqrt{2}}(\theta_{\text{OCH}} - \theta'_{\text{OCH}})
\end{aligned} \tag{10}$$

This quartic force field (QFF) is generated by displacing the equilibrium symmetry-adapted internal coordinates by 0.01 Å for bond lengths and 0.02 rad for bond angles. The displaced internal coordinate configurations are then transformed to the 183 required symmetry unique Cartesian geometries. The focal-point procedure is performed at each of the displaced geometries using the CCSDT(Q)/CBS level of theory. The INTDIF2008 *Mathematica* program[66] is used to generate the single-point geometries, as well as solve for the symmetry-adapted internal coordinate energy derivatives by central finite difference formulae. In the polynomial below, the symmetry-adapted force constants are represented as $\text{F}_{ij} = \frac{\partial^2 V}{\partial S_i \partial S_j}$, $\text{F}_{ijk} = \frac{\partial^3 V}{\partial S_i \partial S_j \partial S_k}$, and $\text{F}_{ijkl} = \frac{\partial^4 V}{\partial S_i \partial S_j \partial S_k \partial S_l}$.

$$\mathrm{V}_4(\mathbf{S}) = \frac{1}{2}\sum_{ij}\mathrm{F}_{ij}S_iS_j + \frac{1}{6}\sum_{ijk}\mathrm{F}_{ijk}S_iS_jS_k + \frac{1}{24}\sum_{ijkl}\mathrm{F}_{ijkl}S_iS_jS_kS_l. \tag{11}$$

The coordinates in Eqn. 11 are understood to be displacement coordinates in **S**. Up to four-mode coupling is considered (unrestricted summations up to fourth order) but force constants obviously related by symmetry are equivalent, such as $\mathrm{F}_{ij} = \mathrm{F}_{ji}$, and only computed once.

Relativistic corrections to the CCSDT(Q)/CBS QFF are evaluated as the difference between the symmetry-adapted internal coordinate force constants (Eqn. 11) from two additional QFFs. These are the ae-CCSD(T)/cc-pCVQZ (MVD2)[56,57] and ae-CCSD(T)/cc-pCVQZ (referred to as nonrel) levels of theory, $\Delta_{\mathrm{rel}} = \mathrm{V}_4(\mathbf{S}_{\mathrm{MVD2}}) - \mathrm{V}_4(\mathbf{S}_{\mathrm{nonrel}})$, where the QFFs in Δ_{rel} are expanded about a geometry optimized at their respective levels of theory. Corrections made directly to the CCSDT(Q)/CBS energy with the same methods, $E_{\mathrm{CBS}}^{\mathrm{CCSDT(Q)}} + (E_{\mathrm{MVD2}} - E_{\mathrm{nonrel}})$, are found inferior to those made at the force constant level due to increasingly large shifts observed in F_{22}, the diagonal C−O stretching force constant. The additive difference corrected CBS geometry, $r_{\mathrm{CBS}+\Delta_{\mathrm{rel}}}$ (Eqn. 5), is used as the equilibrium geometry in VPT2 calculations in both cases but is likely inferior to a geometry which is optimized using a numerical gradient that explicitly contains scalar relativistic corrections. All QFFs are generated in the same procedure described at the beginning of this section and, thus, displace the corresponding CCSDT(Q)/CBS, MVD2, and nonrel equilibrium structures along the same set of internal coordinate displacements. A diagonal Born-Oppenheimer correction (DBOC) was determined negligible for the present work but Refs. 6, 67, and 68 show how the magnitude of DBOCs can grow with the number of vibrational quanta in energy levels of water and how DBOC surfaces are needed for spectroscopic quality results for systems such as H_3^+.

Variational results for anharmonic vibrational frequencies are provided (using the full extrapolated surface) through discrete variable representation (DVR) with P. B. Changala's NITROGEN program.[69] A series of 9, 12, 12, 12, 12, and 9 potential-optimized grid points are chosen for NITROGEN from an initial basis spanning 1.7 Å, 1.2 Å, 1.2 Å, 90°, 90°, 120° in redundant simple internal coordinates (see above). Standard thick restart was used with a Lanczos tolerance of 1.0×10^{-6} cm^{-1} where the reported energy levels are converged to machine precision (approximately 1.0×10^{-12} cm^{-1} in this case). Coordinate transformations are performed with respect to the simple internal bond displacement coordinates, Δr_{CH} and Δr_{CO}, that comprise $S_{i=1-2,5}$ to generate a Morse,[70] $\mu = 1 - \exp(-\alpha\Delta r)$, representation of the PES, $\alpha = -f_{iii}/3f_{ii}$, before prediction of vibrational eigenvalues. The simple internal coordinate derivatives used in α are defined as $f_{ii} = \frac{\partial^2 V}{\partial r_i^2}$ and $f_{iii} = \frac{\partial^3 V}{\partial r_i^3}$. The final surface maintains the symmetry of the original.

Second-order vibrational perturbation theory (VPT2) is used to provide vibrational frequencies and spectroscopic constants with the SPECTRO program[71] based on the quartic potential, $\mathrm{V}_4(\mathbf{q})$. The non-linear transformation of geometric derivatives, required to go from curvilinear internal coordinate space to Cartesian space, is performed using the INTDER2005 program[72] before transformation to reduced normal coordinates.[73]

$$\mathrm{V}_4(\mathbf{q}) = \frac{1}{2}\sum_{r}\omega_r q^2 + \frac{1}{6}\sum_{rst}\phi_{rst}q_r q_s q_t + \frac{1}{24}\sum_{rstu}\phi_{rstu}q_r q_s q_t q_u \tag{12}$$

Additional anharmonic force fields are generated for the CCSD(T)/cc-pVXZ (X=T,Q,5) levels of theory with the procedure noted above where SPECTRO is used to provide vibrational frequencies and anharmonicity constants. The first and second harmonic derivatives are calculated using the GUINEA module of CFOUR 2.0. Fermi resonances are treated in both SPECTRO and GUINEA where results are confirmed consistent to the reported values.

2.6 Recursive Calculation of Response Properties

For the analytic calculation of response properties at the Hartree-Fock (HF) level, a recently developed formulation of response theory[74] and its recursive implementation[75] in a local version of the Dalton2013 program suite[76,77] was employed, where differentiated one- and two-electron integrals were obtained using the Gen1Int[78,79] and cgto-diff-eri[80,81] modules, respectively, and where the response equation solver of Jørgensen *et al.*[82] was used. The method has previously been described extensively,[74,75] and we refer the interested reader to this earlier work for further details about the underlying theory and its implementation. In the present manuscript, we will only outline the main features of the approach.

In this formulation, an arbitrary response property $\langle\langle A; B, C, \ldots\rangle\rangle_{\omega_{bc\cdots}}$ involving perturbations $a, b, c \ldots$, associated with a collection of frequencies $\omega_{bc\cdots}$, where $\omega_a = -\sum_{i\in\{b,c,\ldots\}} \omega_i$, is expressed as a quasienergy derivative $\mathcal{L}^{abc\cdots}_{k,n}$. Using a generalization of Wigner's $(2n+1)$ rule expressed by integers k and n and permitting truncation rule choices between and including the well-known $(n+1)$ and $(2n+1)$ rules,[83] response properties can be expressed compactly as

$$\begin{aligned}\langle\langle A; B, C, \ldots\rangle\rangle_{\omega_{bc\cdots}} = \mathcal{L}^{abc\cdots}_{k,n} \overset{\{\mathrm{Tr}\}_T}{=} E^{abc\cdots}_{k,n} - (\mathbf{SW})^{abc\cdots}_{n_W} - (\mathbf{S}^a\mathbf{W})^{bc\cdots}_{k_S,n'_W} \\ - (\boldsymbol{\lambda}^a\mathbf{Y})^{bc\cdots}_{k_\lambda,n'_Y} - (\boldsymbol{\zeta}^a\mathbf{Z})^{bc\cdots}_{k_\zeta,n'_Z}, \qquad (13)\end{aligned}$$

where E in this work is the HF energy, $\mathbf{S}$ is the overlap matrix, $\mathbf{W}$ is a generalization of the so-called energy-weighted density matrix, and $\boldsymbol{\lambda}$ and $\boldsymbol{\zeta}$ are Lagrange multipliers for respectively the time-dependent self-consistent field and idempotency conditions, expressed as $\mathbf{Y}$ and $\mathbf{Z}$, respectively. The notation $\overset{\{\mathrm{Tr}\}_T}{=}$ signifies that the trace and time-average over the collective oscillation period of the applied perturbations will be taken for the terms on the right-hand side of Eq. (13), and superscripts $abc\cdots$ denotes perturbation-strength differentiation and subsequent evaluation at zero perturbation strength for the collection of perturbations thus indicated. The integers k and n, taking various forms in Eq. (13), indicate a particular choice of the generalized Wigner rule, placing certain conditions on which terms must be evaluated to yield the desired response property. We remark that in this work, which involves only perturbations that represent displacement of the Cartesian coordinates of the system, the maximum value of k and n for a given property notably determines the maximum order of such perturbation to which the density matrix $\mathbf{D}$ and Fock matrix $\mathbf{F}$ must be evaluated during the course of the calculation. For further details, we refer to the original works;[74,75] noting, however, that it is the $(2n+1)$ rule which for all properties in this work will result in the lowest computational costs and is therefore here the one chosen. The $(2n+1)$ rule choice is equivalent to setting $(k,n) = (2,2)$ and $(k,n) = (2,3)$ for the fifth- and sixth-order force constants, respectively, and the fifth-order force constants $\mathcal{L}^{ggggg}$, where g denotes displacement of the Cartesian nuclear coordinates, are thus obtained by evaluating the expression

$$\begin{aligned}\mathcal{L}^{ggggg}_{2,2} \overset{\{\mathrm{Tr}\}_T}{=} {} & E^{ggggg}_{2,2} - (\mathbf{SW})^{ggggg}_{2_W} - (\mathbf{S}^g\mathbf{W})^{gggg}_{2_S,2'_W} \\ & - (\boldsymbol{\lambda}^g\mathbf{Y})^{gggg}_{2_\lambda,2'_Y} - (\boldsymbol{\zeta}^g\mathbf{Z})^{gggg}_{2_\zeta,2'_Z},\end{aligned} \tag{14}$$

for the fifth-rank tensor containing all combinations of the components of such displacements, while the corresponding expression for sixth-order force constants $\mathcal{L}^{gggggg}$ is

$$\begin{aligned}\mathcal{L}^{gggggg}_{2,3} \overset{\{\mathrm{Tr}\}_T}{=} {} & E^{gggggg}_{2,3} - (\mathbf{SW})^{gggggg}_{3_W} - (\mathbf{S}^g\mathbf{W})^{ggggg}_{2_S,3'_W} \\ & - (\boldsymbol{\lambda}^g\mathbf{Y})^{ggggg}_{2_\lambda,3'_Y} - (\boldsymbol{\zeta}^g\mathbf{Z})^{ggggg}_{2_\zeta,3'_Z}.\end{aligned} \tag{15}$$

2.7 4$^{\mathrm{th}}$-order Vibrational Perturbation Theory

Using the recursive approach of the previous subsection, a set of fully analytic HF/cc-pVTZ quintic and sextic geometric derivatives are determined in the Cartesian reference frame with an S_0 H_2CO structure optimized at the HF/cc-pVTZ level of theory. An analytic HF/cc-pVTZ Hessian produced about this equilibrium structure is used to transform the

Cartesian derivatives into a reduced normal coordinate (dimensionless) system. For clarity, CCSDT(Q)/CBS reduced normal coordinates are referred to as **q** whereas HF/TZ reduced normal coordinates are denoted by **q'**. The set of HF/TZ reduced normal coordinate fifth- and sixth-order derivatives determined from the recursive approach is referred to as $\mathrm{V}_6(\mathbf{q'})$ as shown in Eqn. 16.

$$\mathrm{V}_6(\mathbf{q'}) = \frac{1}{120}\sum_{rstu}\phi_{rrstu}q_r^2 q_s q_t q_u + \frac{1}{720}\sum_{rtu}\phi_{rrttuu}q_r^2 q_t^2 q_u^2 \tag{16}$$

Additionally, the improved convergence radius of the aforementioned CCSDT(Q)/CBS Morse-based QFF is exploited to produce another set of reduced normal coordinate force constants up to sixth-order by LSQ fitting energies to displacements along **q**, the CCSDT(Q)/CBS reduced normal coordinates. It may be noted that only the expansion coefficients known to contribute in VPT4 are used to define the quintic and sextic portions of both force fields.

Fundamental frequencies computed with fourth order vibrational perturbation theory (VPT4) are determined using both the quartic ($\mathrm{V}_4(\mathbf{q})$) and quintic and sextic ($\mathrm{V}_6(\mathbf{q})$ or $\mathrm{V}_6(\mathbf{q'})$) force fields, as well as vibrational corrections to the instantaneous moments of inertia $\mu_{\alpha\beta}$. The mass-dependent pseudopotential term $\mathrm{U}(\mathbf{q})$ which appears in the Watson Hamiltonian has not been included fully to fourth order. We use standard Rayleigh-Schrödinger perturbation theory and a direct sum-over-states formalism, in contrast to other work on analytical[84] and numerical[85,86] contact transformations. This approach has been incorporated into the GUINEA module of the CFOUR program suite.[58] VPT4 is also capable of generating additional vibrational corrections to the rotational constants, centrifugal distortion constants, etc. We expect that these additional corrections could account for some of the residual differences with respect to experiment that we observe (see for example, Table 12); however, we have not yet implemented them.

All electronic structure computations are based on restricted Hartree-Fock (RHF) reference wavefunctions. The Molpro 2010.1.67 computational chemistry suite[87] is used for single-point coupled cluster computations up to CCSD(T). One and two electron integral cutoffs are 1×10^{-14} E_h where the HF and coupled cluster energies are converged to 1×10^{-11} E_h. The NCC module[24] of the CFOUR 2.0 package[58] is used for the CCSDT and CCSDT(Q) computations in the spin-adapted non-orthogonal coupled cluster framework.[18] CCSD(T)/aug-cc-pVQZ (aQZ) electronic contributions to the rotational constants of the CCSDT(Q)/CBS reference structure are provided through CFOUR 2.0. Coupled cluster energies and amplitudes are converged to better than 1×10^{-9} E_h in the CFOUR interfaced computations.

3 RESULTS AND DISCUSSION

3.1 Equilibrium Structures and Rotational Constants

The change in predicted geometries is a function of both basis set and treatment of electron correlation.[61,88–93] These trends can be summarized succinctly with respect to the C_{2v} ground state of formaldehyde as: 1) bonds contract and angles grow with increasing basis set cardinality as well as with the inclusion of core correlation; and 2) bonds lengthen and angles shrink slightly as the description of the n-particle space improves. These relationships are explored here using the *ab initio* structures of S_0 H_2CO predicted at various levels of theory as shown in Table 2. The CCSD(T)/TZ predicted structure displays the longest bonds and smallest HCH bond angle; the only unique bond angle in the system due to symmetry. This bond angle widens significantly, from 116.185 to 116.442°, in the CCSD(T)/QZ structure where the characteristic contraction of bond lengths is observed. The contraction is especially prominent in r_e(CO) which decreases by 0.003 Å. The r_e(CO) bond is relatively converged in the included CCSD(T)/cc-pVXZ, X = T, Q, 5, sequence (referred to as T→Q→5 hereafter) at the CCSD(T)/5Z geometry which only shrinks by 0.00024 Å compared to the cc-pVQZ geometry. However, a modest contraction of r_e(CH) is accompanied by an increase in θ_e(HCH) as the basis set grows from cc-pVQZ to cc-pV5Z.

The focal-point gradients used to optimize the CBS structures in this paper rely on extrapolation of CCSD(T)/cc-pVXZ (X=Q,5,6) energies and are corrected for higher-order electron correlation using up to the CCSDT/5Z and CCSDTQ/TZ levels of theory as seen in Eqns. 3 and 4. The $E_{\infty}^{\mathrm{HF}} + \varepsilon_{\infty}^{(\mathrm{T})} + \Delta E_{\mathrm{core}}$ and $\delta E_5^{\mathrm{T}} + \delta E_3^{\mathrm{Q}}$ or $\delta E_4^{\mathrm{T}} + \delta E_3^{(\mathrm{Q})}$ components of the composite energy are anticipated to shift the geometry in opposite directions within the established trends. It is apparent from the results in Table 2 that the former, CBS, components of the composite energy dominate in this context where large contractions of the bond lengths and a modest widening of the HCH bond angle are observed in the CBS results when compared to the CCSD(T)/cc-pVXZ (X=T,Q,5) structures.

The three-point finite difference optimized ae-CCSDT(Q)/CBS geometry correlates all electrons and is used to gauge the error associated with the core correlation correction, ΔE_{core}, used in the frozen core CCSDT(Q)/CBS results. The differences between these two geometries are listed in Table 2 as Err(Δ_{core}). A slight contraction of the bond lengths, as well as HCH bond angle, is observed in the three-point optimized all-electron ae-CCSDT(Q)/CBS results when compared to the three-point optimized CCSDT(Q)/CBS core-corrected structure. Coincidentally, both the r_e(CO) and r_e(CH) bonds are shorter by an equivalent amount of 0.00012 Å and 0.00013 Å, respectively. As such, a core-corrected valence focal point structure may exhibit slightly longer bond lengths and angles than its all-electron counterpart. The three-point and five-point optimized CCSDT(Q)/CBS structures agree within the reported number of significant digits and show negligible differences (deviations on the order of 1×10^{-6} for bond lengths and 1×10^{-4} degrees for bond angles) for the core-corrected results.

The authors are not aware of any previous work which use a more complete composite method than the CCSDTQ/CBS level of theory shown in Eqn. 4 to determine the equilibrium geometry of this system. The energy increments used to correct the CBS energies use basis sets which are two cardinality higher for the iterative triples correction, δE_5^{T}, and one cardinality higher for the iterative quadruples correction, δE_3^{Q}, than previous results.[34] As described earlier in this section, longer bond lengths are expected from more complete models of correlation whereas contractions of these bonds are expected from increases in the cardinality of the basis set. However, Halkier et al. have shown that the iterative triples coupled cluster model (CCSDT) tends to give bond lengths slightly shorter than those of CCSD(T).[94]

Similar behavior is observed here for iterative quadruples upon comparison of the CCSDTQ/CBS and CCSDT(Q)/CBS geometries in Table 2. The CCSDT(Q) model exhibits a slight over-estimation of the total energy as first reported in Bomble et al.'s introduction of the method.[23] Eriksen et al.[95] recently evaluated a number of non-iterative quadruple excitation coupled cluster models and determined the correlation energy recovery of CCSDT(Q), using a cc-pVTZ basis set, to be ∼10% above that of the iterative CCSDTQ model. Thus, the r_e(CO) bond length of the CCSDT(Q)/CBS structure, which is longer than the CCSDTQ/CBS result by 0.00027 Å, is likely a consequence of the overestimation of the quadruples component present in the CCSDT(Q) model. The r_e(CH) bond length and θ_e(HCH) bond angle, on the other hand, appear converged at this level of theory as seen in Table 2.

Despite the well-studied nature of S_0 formaldehyde, there are very few equilibrium structures which are determined at a comparable level of theory as the present results. The equilibrium structure of Puzzarini et al.,[34] shown in Table 3, was determined in a similar method as the present work as it relies on CBS-extrapolated (analytic) gradients which are corrected with an additive difference scheme. Exemplary agreement is seen for the calulated bond lengths of S_0 formaldehyde between the CCSDTQ/CBS structure computed in this work and the cc-pVDZ-based CCSDTQ/CBS structure of Puzzarini et al. The C−O bond length differs by a negligible 0.00003 Å (1.20457 - 1.20454 Å) between the two geometries with an even smaller difference of 0.00002 Å (1.10052 - 1.10050 Å) for the C−H bonds. The assumption of a diminishing basis set dependence for this system is reasonable considering only r_e(CO) shows significant change amongst the CCSDT(Q)/CBS and CCSDTQ/CBS geometries computed in this work.

The convergence of individual structural parameters relies not only on the reported *ab initio* results but also requires validation through empirical findings. At present, Lohilahti reports the most recent (and certain) experimentally derived r_e structure of S_0 formaldehyde.[96] As shown in Table 3, both the CCSDT(Q)/CBS and CCSDTQ/CBS equilibrium structures provided in this work show exceptional agreement with that of Lohilahti's experimental structure. Both CBS geometries fall within experimental uncertainty for the CH bond lengths and HCH bond angle, differing less than 0.0001 Å from experiment in r_e(CH) for both structures. CCSDTQ/CBS predicts a r_e(CO) bond length within experimental uncertainty, only 0.00004 Å from Lohilahti's value, whereas CCSDT(Q)/CBS mildly overestimates the length, landing slightly outside the error bounds. The additive difference relativistic corrections shown in Table 2 and described in the theoretical methods appear effective here in the case of CCSDT(Q)/CBS, moving the corrected geometry closer in every case, with r_e(CO) = 1.20471 Å, r_e(CH) = 1.10042 Å, and θ_e(HCH) = 116.698 degrees. For CCSDTQ/CBS, both the relatively converged CH bond lengths and HCH bond angle improve when including relativistic corrections but the CO bond length moves away from the experimental structure (although still within experimental uncertainty) at r_e(CO) = 1.20444 Å.

Further validation of the quality of the provided structure is found through the analysis of rotational constants. The equilibrium rotational constants, B_e, provided in Table 3 are computed by CFOUR from the internal coordinates of the listed structure if they are otherwise unreported in the corresponding literature. The B_e of the present work are corrected for vibrational and electronic (magnetic) effects as $B_0 = B_e + \Delta B_{\mathrm{vib}} + \Delta B_{\mathrm{el}}$, where B corresponds to A, B, or C, as described in previous work.[34] Vibrational corrections, Δ_{vib}, to the equilibrium rotational constants are determined with VPT2 from the CCSDT(Q)/CBS force field whereas electronic contributions, ΔB_{el}, are predicted at the CCSDT(Q)/CBS geometry using the CCSD(T)/aQZ level of theory. These are ΔA_{vib} = -3235.6 MHz, ΔB_{vib} = -158.7 MHz, and ΔC_{vib} = -303.0 MHz for vibrational corrections and ΔA_{el} = -438.4 MHz, ΔB_{el} = -4.7 MHz, and ΔC_{el} = -1.8 MHz for the magnetic corrections.

The magnetic correction, $\Delta B_{el} = \frac{m_e}{m_p} g B_e$ (m_e and m_p are the masses of an electron and proton, respectively), appears particularly large for A when compared to past studies of halogen cynanides[97] where a correlation between mass and molecular magnetic moment (g-value) was emphasized. In the present case, the electronic contribution to the rotational **g**-tensor dominates the nuclear contribution (especially in the case of the a-principal axis) producing g-values in line with past experimental work.[98] The g-values are g_{aa} = -2.8177, g_{bb} = -0.2201, and g_{cc} = -0.0952 here whereas Flygare[98] reports g_{aa} = -2.9017(8), g_{bb} = -0.2243(1), and g_{cc} = -0.0994(1). Other planar systems with a central double bond show a similar pattern where the g-value along the double bond axis is much larger than the others. This is the case for the isoeletronic methanimine[99,100] (g_{aa} = -1.27099(22), g_{bb} = -0.18975(7), and g_{cc} = -0.03440(8)) as well as the isovalent thioformaldehyde[98] (g_{aa} = -5.6202(68), g_{bb} = -0.1337(4), and g_{cc} = -0.0239(4)). The interested reader is encouraged to review the supporting information of Ref. 34 for a tabulation of *ab initio* ΔB_{el} values for first-row polyatomics and their isotopes.

A recent study of S_0 H_2CO in the terahertz (THz) regime reports high-accuracy A, B, C constants 281970.5558(61), 38833.98715(31), and 34004.24349(31) MHz, respectively.[30] A difference of 42.3, 19.7, and 10.9 MHz is observed between the experimental A, B, and C constants of Brunken et al. and the theoretical A_0, B_0, and C_0 constants of the CCSDT(Q)/CBS structure.[30] This represents a mean absolute percent error (MAPE; shown below where Y is relative to X) of 0.033% with respect to the experimental values.

$$\mathrm{MAPE}(\%) = \frac{100\%}{n}\sum_{i=1}^{n}\left|\frac{X_i - Y_i}{X_i}\right| \tag{17}$$

Improvement on the MAPE is found by applying the same corrections to the equilibrium rotational constants computed using the CCSDTQ/CBS structure. Both B_0 and C_0 show better agreement with B_0 differing by 4.7 MHz and C_0 by 1.0 MHz from experiment but a slight decrease in accuracy is observed in A_0 which varies by 46.9 MHZ. This level of accuracy produces a MAPE a third of the original value at 0.010%. Inclusion of the CCSDT(Q)/CBS quartic and sextic centrifugal distortion constants effects shifts A_0, B_0, and C_0 by 0.0, -1.3, and 1.3 MHz, respectively, which moves both the CCSDT(Q)/CBS and CCSDTQ/CBS rotational constants slightly away from experiment. Although beyond the scope of this work, a better comparison here would be to compute the actual ground state rotational level positions variationally using our potential, and then fit them to the same rotational Hamiltonian used by Brunken et al. However, this would not alter the qualitative result observed here: that the rotational constants computed here via VPT2 are in excellent agreement with experiment. The present VPT4 framework will soon allow for further correction of these spectroscopic constants through higher-order contributions, once implemented, and should provide even more accurate results by refining ΔB_{vib} as well as providing a more complete description of centrifugal distortion.

3.2 Vibrational Band Origins

3.2.1 Convergence of VBOs

The easily applied and well-documented convergence patterns of structural parameters seen in subsection A do not generally extend to the vibrational properties of polyatomic molecules. A number of studies have shown that no systematic trend can be applied to anticipate change associated with basis set cardinality as individual harmonic frequencies may increase or decrease independent of one another.[101–103] However, previous work regarding the effects of electron correlation on the harmonic frequencies of diatomics[89,104] and small polyatomics[105,106] suggest that convergence of ω_i follows that of the energy itself. A very narrow selection of literature exists on the convergence of anharmonic frequencies[36,107–110] due to the cost associated with benchmarking large potential expansions. Most anharmonic force field studies focus on reporting a set of spectroscopic constants which provide the best agreement to experimentally observed VBOs rather than analyze the convergence properties of the system being investigated.

For these reasons, a progression of CCSD(T)/cc-pVXZ (X=T,Q,5) harmonic and anharmonic fundamental vibrational frequencies is shown in Table 4 for S_0 formaldehyde alongside the modern CCSDT(Q)/CBS results. Martin has shown the convergence of ω_i for S_0 H_2CO in the CCSD(T)/cc-pVXZ (X=D,T,Q) sequence.[102] The present CCSD(T)/cc-pVXZ (X=T,Q) results match those of Martin showing an increase in $\omega_1(a_1)$ and $\omega_5(b_2)$ (C$-$H stretching modes) with decreases in $\omega_3(a_1)$, $\omega_4(b_1)$, and $\omega_6(b_2)$ (bending modes) from T→Q. At first sight, it is appealing to assume that the geometric changes associated with increasing basis set cardinality (contraction of bonds and widening of angles) explain these frequency changes on the basis of nuclear-nuclear repulsion. However, such a simple argument is incomplete with respect to the changes seen in $\omega_2(a_1)$ which is dominated by the C=O stretch (86.7% $S_2(a_1)$, 13.7% $-S_3(a_1)$, -0.4% $S_1(a_1)$). Inclusion of the present CCSD(T)/5Z results shows a rise and fall from T→Q→5 in $\omega_2(a_1)$ despite the slightly shorter bond length (0.00023 Å contraction) in the 5Z results relative to the QZ results.

The internal coordinate diagonal quadratic force constants, F_{ii}, provide some insight as they follow directly from the energies and are the dominant terms in the symmetrized **F** matrix.[111] It is obvious from Table 4 that the trends seen in ω_i follow those seen in F_{ii}. The change seen in the T→Q→5 sequence of ω_2 is captured by F_{22} as $13.03486 \rightarrow 13.08516 \rightarrow 13.06267$ aJ/Å^2. Inspection of the CCSDT(Q)/CBS results shows this analysis to be consistent with the aforementioned trend of increases in C$-$H stretching modes and decreases in bending modes with improved basis set. While the F_{22} constant of CCSD(T)/TZ is similar to the CCSDT(Q)/CBS value, the off-diagonal F_{21}, F_{31}, and F_{32} constants in the A_1 symmetry block are larger in the latter CBS-extrapolated results and, thus, care must be taken comparing the magnitudes of force constants outside of a sequence. The internal coordinates used here are representative of the normal modes of vibration of formaldehyde, as a total energy distribution (TED) shows only two vibrational modes, $\omega_2(a_1)$ and $\omega_3(a_1)$, which correspond to <99.9% of the associated symmetry-adapted coordinate. The former has been described above but the latter $\omega_3(a_1)$ is represented by 86.4% $S_3(a_1)$ and 13.4% $S_2(a_1)$ with a miniscule contribution from $S_1(a_1)$. Previous work on ethylene does not reveal a similar relationship between harmonic force constants and frequencies, reinforcing the system specific nature of these properties.[107]

The anharmonicity constants, x_{ij}, comprise contributions from the cubic and quartic PES expansion coefficients and are related to the anharmonic vibrational fundamental frequencies, ν_i, by:[112]

$$\nu_i = \omega_i + 2x_{ii} + \frac{1}{2}\sum_{i\neq j} x_{ij}. \tag{18}$$

Convergence of individual anharmonicity constants in the T→Q→5 progression shows the x_{ii} values steadily decreasing for $i = 1, 2, 5$ and increasing for $i = 3, 4, 6$, suggesting that, in smaller basis sets, diagonal anharmonicity is underestimated for stretching modes and overestimated for bending modes. Both the diagonal and off-diagonal anharmonic corrections (the second and third terms in Eqn. 18, respectively) for the antisymmetric and symmetric C$-$H stretching modes, $\nu_5(b_2)$ and $\nu_1(a_1)$, decrease in the T→Q→5 progression as well as in the CCSDT(Q)/CBS results. These decreases serve to offset the increases seen in $\omega_1(a_1)$ and $\omega_5(b_2)$ but both modes are affected by first-order resonances which affect their overall accuracy as discussed later. The remaning off-diagonal coupling constants do not show a similar trend overall but many x_{ij} tend toward a certain change even into the CCSDT(Q)/CBS results. It should be noted that the CCSD(T)/TZ results show large changes from T→Q relative to the rest of the progression series changes especially in the case of the resonance-affected x_{52} and x_{65} constants. The $\%\omega$ term listed in Table 4 is defined as $(1 - \nu/\omega) * 100\%$ and describes the anharmonicity of the fundamental with respect to its corresponding harmonic frequency.

3.2.2 VPT2 and the $5_1, 2_1 6_1, 3_1 6_1$ Triad

The treatment of anharmonic resonances which affect the vibrational frequencies of a molecule in VPT2 involves two steps; the reformulation of affected anharmonicity constants, x_{ii} and/or

x_{ij}, to accomodate the removal of resonance denominators (or the equivalent sum-over-states alternative) and the subsequent diagonalization of an effective Hamiltonian which contains the deperturbed frequencies along with appropriate interaction constants.[112–116] Resonance interactions are most often identified in a VPT2 analysis by the differences in the energy of symmetry-related combinations of harmonic vibrational frequencies which correspond to first-order (Fermi) and second-order resonances. However, critical interactions which may otherwise cause large shifts in the anharmonicity constants and, thus, anharmonic vibrational frequencies may be overlooked due to arbitrarily defined tolerances.[116] The CCSDT(Q)/CBS fundamentals of S_0 formaldehyde serve as an example of this concept where a generous threshold of 200 cm^{-1} would fail to identify the well-documented[2,29] $\omega_3(a_1)+\omega_6(b_2) \approx \omega_5(b_2)$, 1534.91 + 1271.10 $\approx$ 3008.63 cm^{-1}, component of the $5_1, 2_16_1, 3_16_1$ resonance triad as $\Delta\omega = 202.62$ cm^{-1}. It is interesting to note that the failure of this detection method for S_0 formaldehyde is an emergent property of the high-level CBS treatment as the previously mentioned convergence pattern of the harmonic frequencies pushes $\Delta\omega$ beyond the (arbitrary but oft-applied) threshold.

A complete description of this three-state interaction in VPT2 requires the diagonalization of the effective Hamiltonian, $\mathbf{H}_{\text{eff}}$, shown in Eqn. 19. The diagonal terms correspond to the deperturbed values of the corresponding energies and are denoted with an asterisk where combination levels are determined as $\nu_i+\nu_j+x_{ij}$. Off-diagonal matrix elements serve as a measure of coupling between states where first-order interaction constants easily follow from the cubic force constants. A trivial representation of the matrix element describing the second-order interaction between the 2_16_1 and 3_16_1 combination levels, denoted K below, is

$K = 0$ as the coupling between these two states is expected to be limited.[115]

$$\mathbf{H}_{\text{eff}} = \begin{array}{c} \\ \\ \end{array} \begin{array}{ccc} 5_1 & 2_16_1 & 3_16_1 \\ \end{array}$$

$$\mathbf{H}_{\text{eff}} = \begin{pmatrix} \nu_5^* & \frac{1}{\sqrt{8}}\phi_{652} & \frac{1}{\sqrt{8}}\phi_{653} \\ \frac{1}{\sqrt{8}}\phi_{652} & \nu_2 + \nu_6 + x_{62}^* & K \\ \frac{1}{\sqrt{8}}\phi_{653} & K & \nu_3 + \nu_6 + x_{63}^* \end{pmatrix} \tag{19}$$

However, a more thoughtful solution to the matrix element denoted by K, shown in Eqn. 20, follows from the second-order contact transformation. Such relationships have been carefully explored elsewhere.[115,117–120]

$$K = \frac{1}{4}(K_{21,31} + K_{22,23} + K_{23,33} + K_{24,34} + K_{25,35} + 3K_{26,36}) \tag{20}$$

The expression above can be derived from the 1-1 resonance equations found in Ref. 119 where the necessary numerical factors follow from harmonic oscillator matrix elements in reduced normal coordinates.

The eigenvalue of Eqn. 19 whose largest eigenvector coefficient belongs to the 5_1 state is listed in Table 11 for both solutions of K alongside the contributions (coefficients squared) from the other two states for the non-trivial K solution of $\mathbf{H}_{\text{eff}}$. A complete treatment of the $5_1, 2_16_1, 3_16_1$ resonance triad through deperturbation of $5_1 \approx 2_16_1$ and $5_1 \approx 3_16_1$ followed by the diagonalization of $\mathbf{H}_{\text{eff}}$ in Eqn. 19 provides a superior result for $\nu_5(b_2)$ only in the case of the CCSD(T)/TZ data where the trivial solution of K provides the best experimental agreement as discussed in the following section. McCaslin et al. have recently produced the Full K solutions of $\nu_5(b_2)$ for CCSD(T)/XZ (X = D, T, Q) as well as benchmarking the more complete NASA Ames atomic natural orbital (ANO) basis sets.[121] The Full K solutions in Table 11 match the fundamental values reported by McCaslin et al. for CCSD(T)/XZ (X = T, Q) where the current work extends the data to show convergence onto the CCSDT(Q)/CBS result of 2850.05 cm^{-1}. The CCSD(T)/ANO0 (2855 cm^{-1}) and

CCSD(T)/ANO2 (2852 cm^{-1}) results of McCaslin et al. are in excess of the CCSD(T)/CBS result but the CCSD(T)/ANO1 $\nu_5(b_2)$ value of 2849 cm^{-1} is promising. In either case, the ANO basis sets suffer from the same overestimation of $\nu_5(b_2)$ relative to experiment, without exception, when using the full treatment of the Fermi resonance.

The treatment of isolated Fermi ($\nu_i \sim 2\nu_j$ and $\nu_i \sim \nu_j + \nu_k$) resonances in VPT4 is a straightforward extension of the treatment for VPT2: the diagonal elements of the effective Hamiltonian are deperturbed VPT4 energies, and the off-diagonal element is the sum of the first- and third-order Hamiltonian matrix elements. For formaldehyde, the coincidence of the $5_1 \sim 2_1 6_1$ and $5_1 \sim 3_1 6_1$ Fermi resonances requires inclusion of an off-diagonal Darling-Dennison term (the K term in VPT2). For VPT4, this requires evaluation of the fourth-order once-transformed off-diagonal Hamiltonian, which we have not yet derived. Instead, we substitute the second-order K constants, as this coupling element has a rather small effect on the diagonalized energies. The interaction between $\nu_1(a_1)$ and $2\nu_4(a_1)$ is relatively weak with $\Delta\omega = 133.76$ cm^{-1} but is included as a Fermi resonance in the following VPT2 and VPT4 analysis as its treatment as such improves agreement to experiment in both cases.

3.2.3 Comparison to Experiment

Comparison to previous theoretical and experimental work of S_0 H_2CO's fundamental frequencies is shown in Table 5. Theoretical results are evaluated against the analysis of Tchana et al.[122] and Bouwens et al.[29] It is clear from the VPT2 results that as basis set cardinality increases in the CCSD(T)/cc-pVXZ (X = T, Q, 5) sequence that the individual errors relative to experiment are reduced or left unchanged as in the case of $\nu_6(b_2)$. The exception to this is $\nu_5(b_2)$ which is involved in the aforementioned $5_1, 2_1 6_1, 3_1 6_1$ resonance triad where the large difference seen between CCSD(T)/TZ and CCSD(T)/QZ are emphasized in previous sections and detailed in Table 11. Overall error decreases despite this exception as evidenced by the MAEs ($\frac{1}{n}\sum_{i=1}^{n}|X_i - Y_i|$) and MAPEs (Eqn. 17).

Extrapolation to the basis set limit with corrections for higher-order dynamic and core correlation, as represented by the CCSDT(Q)/CBS level of theory, shows a significant improvement in most but not all fundamentals. Substantial decreases in the absolute errors of the C−O stretch, $\nu_2(a_1)$, and torsion, $\nu_4(b_1)$, which drop from 1.97 to 0.47 cm^{-1} and 1.47 to 0.14 cm^{-1}, respectively, are seen when moving from the CCSD(T)/5Z to CCSDT(Q)/CBS results. The accuracy of the anti-symmetric OCH bend, $\nu_6(b_2)$, and symmetric C−H stretch, $\nu_1(a_1)$, improve by similar amounts where error is reduced by over half a wavenumber. Comparable accuracy is observed in both the CCSDT(Q)/CBS and CCSD(T)/5Z results for the symmetric OCH bend, $\nu_3(a_1)$, where errors for both are approximately a quarter wavenumber (but on either side) from the experimental result of 1500.1747(4) cm^{-1}. Keeping with the trend of increasing error with increasing basis set cardinality, the CCSDT(Q)/CBS VPT2 prediction of $\nu_5(b_1)$ shows the worst agreement to experiment of the included results but of course this is a resonant fundamental. Despite this, the MAE of the CCSDT(Q)/CBS VPT2 fundamentals approach spectroscopic accuracy at 1.49 cm^{-1} where the MAPE is approximately halved relative to the CCSD(T)/5Z results.

The CCSDT(Q)/CBS anharmonicity constants produced in the VPT2 analysis are shown in Table 8. The results vary in accuracy relative to the experimental values reported by Reisner et al.[26] Some constants are surprisingly well-described, such as the x_{22}, x_{42}, x_{44} where the CCSDT(Q)/CBS value of x_{42}, -7.19 cm^{-1}, reproduces Reisner et al.'s experimental value of -7.199(39) cm^{-1}. The utility of this agreement is obvious, as the CCSDT(Q)/CBS prediction of the $2_1 4_1(b_1)$ combination level is 2905.46 cm^{-1} compared to the experimental value of 2905(1) cm^{-1}. However, perfect agreement to Reisner et al.'s derived constants is unnecessary to successfully predict extremely accurate combination levels as exhibited by the VPT2 prediction of $2_1 3_1(a_1)$. The x_{23} constant varies by 1.19 cm^{-1}, nearly 20%, from Reisner et. al.'s result yet a CCSDT(Q)/CBS prediction of $2_1 3_1(a_1)$ at 3238.40 cm^{-1} is only 0.06 cm^{-1} away from the experimental result of 3238.4548(20) cm^{-1} of Perrin et. al.[123]

A better example of this point, and the difficulties associated with the empirical determination of anharmonicity, comes from the $4_1 6_1(a_2)$ and $1_1 6_1(b_2)$ energy levels whose x_{ij}'s are wildly different from their experimental counterparts with x_{64} = 7.07 v.s. -2.860(70) cm^{-1} and x_{61} = -8.37 v.s. -49.78(33) cm^{-1}. CCSDT(Q)/CBS predicts $4_1 6_1 (a_2)$ at 2423.14 cm^{-1} from VPT2 which is only 0.17 cm^{-1} from the high-resolution observations of Perrin et. al.[123] despite x_{64} having the opposite sign and being over twice the magnitude of Reisner et. al's empirical value. Reisner et. al's x_{61} constant is six times that of the CCSDT(Q)/CBS result yet the CCSDT(Q)/CBS $1_1 6_1 (b_2)$ prediction of 4023.46 cm^{-1} is only a couple wavenumbers from Flaud et. al.'s gas phase observation[124] at 4021.08066(60) cm^{-1}. It is not surprising that these two empirically determined anharmonicity constants vary so much from the current high-accuracy study, as Reisner et. al. had to determine five and eleven x_{ij}'s before extracting x_{64} and x_{61}, respectively, where the analysis relied on accurate assignment of the $1_1 4_2 6_1 (b_2)$ and $3_1 4_3 6_1 (a_2)$ combination levels. A more updated fit of the anharmonicity constants is found from Bouwens et. al.[29] which is shown in Table 8 but the agreement is similar and the conclusion remains with regard to theoretical and empirical findings. The present data serves as an excellent example, along the lines of previous work in the literature,[115] of how high-accuracy *ab initio* force fields relying on convergent quantum chemistry can use VPT2 to its fullest by generating a set of spectroscopic constants with predictable accuracy and leverage this in the determination of overtones and combination bands.

The obvious exception to this statement is resonance-affected energy levels where vibrational perturbation theory encounters difficulties that inevitably affect the accuracy of predictions. As previously discussed, the $\nu_5(b_2)$ fundamental is a classic case of this and is qualitatively inaccurate if its interaction with the $2_1 6_1 (b_2)$ and $3_1 6_1 (b_2)$ combination levels is treated with VPT2. The accuracy of the energy levels directly involved in the triad benefits from an effective Hamiltonian treatment (as shown in Eqn. 19) following deperturbation, but x^*_{25}, x^*_{35}, and x^*_{65} and their corresponding unmixed energy levels do not. Errors are over 40 cm^{-1} for CCSDT(Q)/CBS VPT2 predictions of $3_1 5_1 (b_2)$ = 4289.28 cm^{-1} and $5_1 6_1 (a_1)$ = 4042.24 cm^{-1} relative to the gas-phase observations of 4335.09709(60) and 4083.1(10) cm^{-1}, respectively.[29,124] Even the errors for the eigenvalues of $\mathbf{H}_{\text{eff}}$ are far too high relative to the rest of the dataset. Only $2_1 6_1(b_2)$ shows error under 5 cm^{-1} from experiment with a prediction of 3003.79 cm^{-1} which is 3.73 cm^{-1} from the experimental value[26] of 3000.0656(10) cm^{-1}. The relative lack of accuracy in the prediction of resonance-affected energy levels with VPT2 logically leads to variational approaches for predicting vibrational energy levels.

Variational (DVR) solutions to the CCSDT(Q)/CBS vibrational energy levels are shown in Table 5 below their VPT2 counterparts. Individual errors are equivalent or superior to VPT2 for all fundamentals but $\nu_4(b_1)$, the torsional mode, which displays an increase from 0.14 to 0.80 cm^{-1}. Predicted values for $\nu_3(a_1)$ and $\nu_6(b_2)$ are essentially exact with the CCSDT(Q)/CBS potential, where errors are both 0.03 cm^{-1}. The largest error is seen in the C−H stretching modes which are 1.18 and 1.06 cm^{-1} for $\nu_1(a_1)$ and $\nu_5(b_2)$, respectively. The error in $\nu_5(b_2)$ is vastly improved relative to the 6.71 cm^{-1} error from the CCSDT(Q)/CBS VPT2 fundamental, which can largely be attributed to issues associated with treating the resonance discussed earlier. Excellent agreement is seen for the fundamentals overall with a MAE of 0.57 cm^{-1} where the MAPE is half that of the VPT2 results. It is important to recognize these results are exemplary for purely *ab initio* predictions of VBOs, especially for a QFF, but modern high-resolution spectroscopy experiments are capable of obtaining far more accurate rovibrational results for simple systems such as formaldehyde. The beauty of the present work presents itself in situations where experiment cannot isolate, detect, or analyze the molecular species of interest. CCSDT(Q)/CBS VPT2 and DVR fundamentals of D_2CO and HDCO are shown in Table 7.

It should be noted that the original quartic expansion in symmetry-adapted internal coordinates is completely unsuitable for variational solutions to the vibrational problem here. Originally, transformation of the PES to Simons-Parr-Finland (SPF) coordinates was performed but the error was found to be too high for $\nu_1(a_1)$ and $\nu_5(b_2)$, the C−H stretching fundamentals. Rauhut has reported this exact issue previously with variational approaches using many-mode expansions, noting the C−H stretching fundamentals of formaldehyde were sensitive to vibrational coupling and prone to errors which were associated with an incomplete description of the potential in its outer regions.[125] Morse coordinates are found to be superior for providing quantitatively accurate, spectroscopic, predictions of the fundamentals; a topic which has been studied previously.[37,126]

3.2.4 Comparison to Previous Theory

There are no known PESs which use high levels of theory (those including CBS extrapolations and higher-order dynamic electron correlation) for this system. Previous theoretical work on formaldehyde is extensive but generally limited to CCSD(T) using the (aug-)cc-pVTZ or (aug-)cc-pVQZ basis sets. It is clear from the variation seen in the error of previous *ab initio* results (Table 5) that the accuracy of predicted VBOs goes beyond choice of theory alone; the form of the PES and solution of the vibrational energy levels is equally important. Results from three types of PES are compared to those of this work: the CCSD(T)/aTZ (and F12b variant) 3-mode (many-mode) expansion of Rauhut et al.,[125,127] which relies on interpolation of intrinsic potentials, the CCSD(T)/TZ SPF QFF of Martin et al.,[65] and the CCSD(T)/aQZ Morse coordinate 6D (full-dimensionality) PES of Yachmenev et al.[5] Almost the entire literature on S_0 formaldehyde (that compares to experimental observations) uses variational approaches for nuclear motion to avoid the resonance denominator issue associated with VPT2.

None of the previous *ab initio* results show accuracy comparable to the present CCSDT(Q)/CBS DVR fundamental VBOs which have a MAE of 0.57 cm^{-1} relative to gas-phase observations. The variational CCSD(T)-F12b/aTZ many-mode results of Rauhut et al. have a respectable MAE of 2.49 cm^{-1} but show the greatest range of error of any of the included results and actually performs worse than its traditional CCSD(T)/aTZ counterpart in predicting an accurate value of $\nu_5(b_2)$ (errors of 6.07 cm^{-1} and 0.27 cm^{-1}, respectively). The *ab initio* CCSD(T)/aQZ 6D PES of Yachmenev et. al., on the other hand, proves more consistent with a MAE of 1.47 cm^{-1} despite unusually large error in the torsion, $\nu_4(b_1)$, of 3.49 cm^{-1}. Such performance is similar to the resonance-affected CCSDT(Q)/CBS VPT2 results (MAE = 1.49 cm^{-1}) where the Yachmenev et. al.'s 6D PES addresses challenges previously noted by Rauhut by using a far more expansive surface and full unconstrained coupling between vibrational modes.[125] A more relevant comparison would be beteween the variational results, DVR and TROVE, where the CCSDT(Q)/CBS QFF clearly shows its strength with a MAE less than half that of the *ab initio* 6D PES.

Fitting of the expansive full-dimensionality 6D surface of Yachmenev et al. to high-quality experimental results is understandably superior to all of the included *ab initio* VBO predictions[5] where MAE relative to experiment is an order of magnitude better than the purely *ab initio* sources. Constructing a semi-empirical PES such as this one obviously requires a great deal of high-resolution gas-phase observations in tandem with significant refinement and is a service to theorists and experimentalists alike, but such treatments are only available for extensively studied and small chemical species. The fact that spectroscopically accurate VBOs can be variationally computed for fundamentals using an unaltered, purely *ab initio*, surface that spans only 183 geometries is quite agreeable when compared to the 30840 geometries used by Yachmenev et al. Moreso, the CCSDT(Q)/CBS DVR results carry a MAE which is only twice that of the semi-empirical fit of Burleigh et al. which relies on the older SPF QFF of Martin et al.[2,65] Individual errors from CCSDT(Q)/CBS DVR are actually superior in some cases ($\nu_3(a_1)$, $\nu_6(b_2)$) to those predicted variationally with canonical Van Vleck vibrational perturbation theory (CVPT) using Burleigh et al.'s empirically fit QFF. An interesting topic for further study would be investigating the accuracy of a semi-empirical QFF produced through refinement of the CCSDT(Q)/CBS QFF used here.

3.2.5 Relativistic Corrections to the PES

Results for fundamental vibrational frequencies using Δ_{rel} corrections to the CCSDT(Q)/CBS equilibrium geometry and PES are shown in Table 5. A negligible decrease of 0.05 cm^{-1} in the error of $\nu_3(a_1)$ is met with increased error in all other fundamentals with the exception of $\nu_5(b_2)$ which is lowered by approximately 0.5 cm^{-1}; a very small effect considering the convergence of the $\nu_5(b_2)$ eigenvalue of $\mathbf{H}_{\text{eff}}$ as shown in Table 11. Closer inspection of the results shows that the magnitude of the shifts between CCSDT(Q)/CBS and the CCSDT(Q)/CBS+Δ_{rel} results are largest in the Fermi-affected C−H modes ($\nu_1(a_1)$, $\nu_5(b_2)$) and, most importantly, the C−O stretch ($\nu_2(a_1)$). The latter fundamental, $\nu_2(a_1)$, drops from 1745.54 to 1744.53 cm^{-1} which increases the error against the experimental value of 1746.00928(49) cm^{-1} by 1.01 cm^{-1}. Such a shift is almost entirely explained by the change in the harmonic force constant of the C−O stretching coordinate, $\Delta_{\text{rel}}(\text{F}_{22})$ = -0.01605 aJ/Å^2, which lowers the harmonic vibrational frequency of 1776.83 to 1775.85 cm^{-1}; almost exactly a wavenumber. The Morse-based variational CCSDT(Q)/CBS+Δ_{rel} predictions behave similarly to VPT2 with respect to the increased error in the C−O stretch ($\nu_2(a_1)$) but, unlike VPT2, the Δ_{rel} shifts to $\nu_1(a_1)$ and $\nu_5(b_2)$ vastly improve agreement to experiment as these modes are predicted with equivalent accuracy in the absence of resonance problems.

3.2.6 4$^{\text{th}}$-order Vibrational Perturbation Theory

VPT2 is a successful, and the most used, approach to vibrational anharmonicity in molecular physics. It is exceptionally easy to use in conjunction with Taylor series representations of the potential energy surface and is familiar to theorists and experimentalists alike. Perhaps VPT2's most obvious limitation is quasi-degeneracies (resonances) but the effective Hamiltonian approach is a solution, albeit an imperfect one, to that problem. What VPT2 cannot do is take advantage of more expansive swaths of the nuclear potential which can be used to produce better predictions of vibrational energy levels. A natural extension to higher-order contributions (those arising from derivatives beyond quartic in normal coordinates) of the PES follows by taking VPT to 4$^{\text{th}}$-order *via* VPT4.

VPT4 requires derivatives of the potential through sextic. Most quantum chemistry packages do not have the automated generation of quartic force fields implemented, let alone to sextic, making the production of these surfaces a challenge. The neccessary quintic and sextic geometric derivatives can be calculated at the HF level by a routine execution of the recursive response theory implementation described in Section 2.6. This is one of the few, if not the only, method(s) of providing arbitrary-order force constants without recourse to numerical methods which are much less reliable at high order than their analytic counterparts. It is straight-forward to extend existing force fields in this way to generate a mixed-theory sextic force field such as the $V_4(\mathbf{q})$[CCSDT(Q)/CBS] + $V_6(\mathbf{q'})$[HF/TZ] one used here. Another strategy used in this study is to LSQ fit displacements along the CCSDT(Q)/CBS reduced normal coordinates ($\mathbf{q}$) to energies from the Morse-based symmetry-adapted internal coordinate QFF to generate $V_6(\mathbf{q})$[CCSDT(Q)/CBS] directly.

The difference in VPT4 vibrational energy levels predicted with these PES is shown as ΔVPT4‡ in Table 6, where VPT4† are the Morse-based results and VPT4‡ are the results relying on the recursively solved $V_6(\mathbf{q'})$[HF/TZ] (see theoretical details). Only the fundamentals, overtones, and combination level of $\nu_2(a_1)$ and $\nu_4(b_1)$ show agreement under a wavenumber between the two VPT4 datasets. The exception to this is the $2_1 6_1(b_2)$ combination level which is part of the discussed resonance triad with $\nu_5(b_2)$ and qualitatively incorrect in VPT. Overall, HF/TZ does not describe the required quintic and sextic regions of the force field with enough accuracy to improve upon the CCSDT(Q)/CBS VPT2 results as most levels are shifted further away from experimental observations in the corresponding VPT4‡ results.

It is immediately obvious from Table 6 that the differences between the DVR and Morse-based VPT4† data is much smaller than those between the two VPT4 datasets, and that between VPT2† and VPT4†. Excellent agreement is anticipated due to the construction of the VPT4† PES through LSQ fitting, and is indeed observed. VPT4 predicts vibrational energy levels virtually identical to those from exact (variational) methods based on the same potential. An order of magnitude increase in agreement is seen between the DVR fundamentals and those predicted from VPT4† when compared to VPT2† for non-resonant levels (to include multi-quanta states). Large shifts from VPT2† to VPT4† in $4_2(a_1)$ and $6_2(a_1)$ clearly show that a lack of vibrational anharmonicity in VPT2 is reponsible for the disagreement with DVR and not a resonance interaction.[29] The treatment of resonances in VPT4 is an open topic but a successful approach has been applied here. Extending the effective Hamiltonian treatment from VPT2 to VPT4 is done by defining the Fermi-interaction terms as the sum of the first-order and third-order Hamiltonian elements while retaining the transformed second-order term (discussed in previous sections) that couples combination levels, if present. Determination of the VPT4 $\nu_5(b_2)$ fundamental in this way shows a value of 2852.11 cm^{-1} which is a vast improvement on the original value of 3105.16 cm^{-1}. The VPT4 Fermi resonance treatment of the questionable interaction between $1_1(a_1)$ and $4_2(a_1)$ slightly improves ($\sim$0.2 cm^{-1}) experimental agreement over the VPT2 result as 2782.25 cm^{-1}.

4 CONCLUSIONS

The application of CCSDT(Q)-based focal-point analysis[14–16] to geometric energy derivatives is now feasible due to the implementation and optimization of non-orthogonal spin-adapted coupled cluster theory.[18,24,25] Optimization of the equilibrium geometry of S_0 formaldehyde using numerical CCSDT(Q)/CBS and CCSDTQ/CBS gradients provides structures that show smooth convergence patterns expected of the quantum chemical methods which define the composite focal-point energy. The gradient-based approach allows high-level geometries to be produced in a straightforward way without fitting structural parameters to a PES at an equivalent level of theory. A brief derivation of how CBS extrapolation formulae may be applied to analytic forms of the molecular gradient is provided to allow subsequent studies to benefit from currently implemented formulations and further advances in the development of high-level coupled cluster approaches.

The CCSDT(Q)/CBS anharmonic force field based on focal-point energies shows the best experimental agreement to date for purely *ab initio* fundamental VBOs of S_0 H_2CO with a MAE of 0.57 cm^{-1} and MAPE of 0.029%. Fermi resonances which affect the fundamentals of S_0 have been explored in detail with emphasis on the interesting emergent behavior of the $5_1, 2_1 6_1, 3_1 6_1 (b_2)$ triad at the CCSDT(Q)/CBS level of theory. A series of anharmonic force fields at the CCSD(T)/cc-pVXZ (X=T,Q,5) levels of theory show that the system-specific basis set convergence of harmonic vibrational frequencies, anharmonicity constants, and their anharmonic counterparts leads smoothly to the current high-level CBS-extrapolated results. A full set of spectroscopic constants computed at the CCSDT(Q)/CBS level which include rotational, centrifugal distortion, and vibration-rotation interaction constants provides a point of comparison for previous and future work. The availability of fully analytic arbitrary-order HF force constants through the recently published recursive approach contributes to the ability to evaluate vibrational perturbation theory corrections beyond second order without recourse to finite difference methods.

The results provided here are proof of concept that state-of-the-art quantum chemistry is capable of providing very accurate (within $\sim$1 cm^{-1} of experiment) fundamental positions of a prototypical tetra-atomic system using a very small PES (183 geometries) which is defined by high-level composite energies. This accuracy is obtained without the use of smaller auxiliary corrections normally seen in composite schemes reiterating that the critical components of any composite method resides in the CBS extrapolation(s) and core correlation treatment. The present purely *ab initio* results rival last-generation empirically fit PES where the theory presented here may lead to unprecedented levels of accuracy through empirical refinement in the future. The obvious advantage of the present, purely *ab initio*, approach over semi-empirical PES is that it enables high-throughput production of accurate geometric and spectroscopic data which has zero experimental reliance using the most trusted, time-tested, methods in quantum chemistry. It is the hope of the authors that the present work provides sufficient example of the capabilities of well-defined *ab initio* methodologies which display easily understood convergence properties and that the methods will be applied to less understood molecules in the future.

5 SUPPORTING INFORMATION

The Cartesian and symmetry-adapted internal coordinate derivatives for the CCSDT(Q)/CBS QFF as well as the CFOUR VPT2 and VPT4 files for the Morse-fit and response theory based sextic force fields are provided in the supporting information. This information is available free of charge via the Internet at http://pubs.acs.org

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Table 1: Example Focal Point Table of CCSDT(Q)/CBS Energies

Basis Set	E_e [RHF]	$+\delta$ [MP2]	$+\delta$ [CCSD]	$+\delta$ [CCSD(T)]	$+\delta$ [CCSDT]	$+\delta$ [CCSDT(Q)]	$= E_e$ [Final]
cc-pVTZ	$\boldsymbol{E_3}$	E_3	E_3	E_3	E_3	$\boldsymbol{E_3}$	E_3
cc-pVQZ	$\boldsymbol{E_4}$	E_4	E_4	$\boldsymbol{E_4}$	$\boldsymbol{E_4}$	$\tilde{E}_4$	$\tilde{E}_4$
cc-pV5Z	$\boldsymbol{E_5}$	E_5	E_5	$\boldsymbol{E_5}$	$\tilde{E}_5$	$\tilde{E}_5$	$\tilde{E}_5$
cc-pV6Z	$\boldsymbol{E_6}$	E_6	E_6	$\boldsymbol{E_6}$	$\tilde{E}_6$	$\tilde{E}_6$	$\tilde{E}_6$
CBS limit	E_∞	E_∞	E_∞	E_∞	$\tilde{E}_\infty$	$\tilde{E}_\infty$	$\tilde{E}_\infty$
Fit	$a + bc^{-eX}$	$a + bX^{-3}$	$a + bX^{-3}$	$a + bX^{-3}$	additive	additive	
Points (X)	4,5,6	5,6	5,6	5,6			

Colored areas are provided using the fit and points in the last two rows or by additivity. Bolded terms are the only energies required to compute the focal-point extrapolated energy. Additive terms are determined as CC$_n$/cc-pVXZ = CC$_{n-1}$/cc-pVXZ + [CC$_n$/cc-pV(X-1)Z - CC$_{n-1}$/cc-pV(X-1)Z] where CC$_{n-1}$ is the previous method in the hierarchy.

Table 2: Computed *ab initio* H_2CO Geometries (Å,°)

Method	Basis	Gradient	r_e(CO)	r_e(CH)	θ_e(HCH)
CCSD(T)	cc-pVTZ	Analytic	1.209 57	1.103 28	116.185
CCSD(T)	cc-pVQZ	Analytic	1.206 58	1.102 18	116.442
CCSD(T)	cc-pV5Z	Analytic	1.206 34	1.101 79	116.597
ae-CCSDT(Q)	CBS	3-point	1.204 62	1.100 40	116.688
CCSDT(Q)	CBS	3-point	1.204 84	1.100 53	116.695
CCSDT(Q)	CBS	5-point	1.204 84	1.100 53	116.695
CCSDTQ	CBS	5-point	1.204 57	1.100 52	116.694
Err(Δ_{core})			-0.000 12	-0.000 13	-0.007
Δ_{rel}			-0.000 13	-0.000 11	+0.004

Frozen core computations unless otherwise denoted as all-electron (ae).
Err(Δ_{core}) = ae-CCSDT(Q)/CBS- CCSDT(Q)/CBS
Δ_{rel} = ae-CCSD(T)/pCVQZ (MVD2) - ae-CCSD(T)/pCVQZ

Table 3: Equilibrium Molecular Structures (Å,°) of $\tilde{X}$ $^1A_1(S_0)$ H_2CO

	Present Work		Rauhut[a]	Puzzarini[b]	Carter[c]	Yachmenev [d]	Experiment[e,f]
	CCSDT(Q)/CBS	CCSDTQ/CBS	*ab initio*	*ab initio*	Spec. Fit	Spec. Fit	
r_e(CO)	1.204 84	1.204 57	1.206 0	1.204 54	1.202 96	1.203 67	1.204 61(19)
r_e(CH)	1.100 53	1.100 52	1.101 9	1.100 50	1.100 64	1.102 90	1.100 46(16)
θ_e(HCH)	116.694	116.694	116.66	116.690	116.704	116.438	116.722(93)
A_e	285 686.8	285 691.3	285 082.7	285 715.9	285 600.5	285 248.4	285 598.2
B_e	38 977.7	38 992.9	38 896.2	38 994.4	39 086.7	38 997.2	38 996.8
C_e	34 298.2	34 310.0	34 226.4	34 311.6	34 381.4	34 307.0	34 308.6
A_0	282 012.8	282 017.3	-	282 033.7	281 955.8	-	281 970.557 8(61)
B_0	38 814.3	38 829.5	-	38 832.1	38 846.3	-	38 833.987 15(31)
C_0	33 993.4	34 005.2	-	34 008.0	34 003.8	-	34 004.243 49(31)

[a] CCSD(T)-F12b/aQZ result from Ref. 127. [b] CCSDTQ/CBS result from Ref. 34.

[c] CCSD(T)/TZ results from Ref. 65 fit to spectroscopically observed vibrational lines in Ref. 4.

[d] CCSD(T)/aQZ PES result fit to spectroscopically observed vibrational lines from Ref. 5.

[e] Experimentally derived equilibrium results from Ref. 96.

[f] A, B, and C from THz and IR results fit to the S reduction in Ref. 30.

Table 4: Basis Set Dependence of S_0 H_2CO VBOs

Theory	5 (b_2)*	1 (a_1)*	2 (a_1)	3 (a_1)	6 (b_2)	4 (b_1)
CCSDT(Q)/CBS						
F_{ii}	4.803 847	4.957 790	13.036 335	1.657 386	0.821 508	0.262 751
w_i	3 008.63	2 936.05	1 776.83	1 534.91	1 271.10	1 186.70
$2x_{ii}$	−75.16	−64.14	−19.53	−1.51	−3.89	−5.62
$\frac{1}{2}\sum_{i\neq j} x_{ij}$	−109.50	−89.04	−11.76	−33.47	−18.26	−13.97
ν_i	2 823.98	2 782.87	1 745.54	1 499.93	1 248.96	1 167.11
$\%w$	6.14	5.22	1.76	2.28	1.74	1.65
CCSD(T)/cc-pV5Z						
F_{ii}	4.797 530	4.952 077	13.062 667	1.662 347	0.823 216	0.263 664
w_i	3 006.43	2 934.70	1 779.05	1 535.16	1 271.10	1 188.18
$2x_{ii}$	−74.58	−63.93	−19.25	−1.31	−4.32	−5.61
$\frac{1}{2}\sum_{i\neq j} x_{ij}$	−108.91	−88.67	−11.82	−33.39	−18.51	−13.85
ν_i	2 822.93	2 782.09	1 747.98	1 500.45	1 248.27	1 168.73
$\%w$	6.10	5.20	1.75	2.26	1.80	1.64
CCSD(T)/cc-pVQZ						
F_{ii}	4.789 586	4.947 730	13.085 162	1.670 461	0.825 754	0.264 194
w_i	3 003.69	2 933.52	1 781.45	1 537.64	1 272.90	1 190.25
$2x_{ii}$	−74.36	−63.85	−19.20	−1.43	−4.38	−5.84
$\frac{1}{2}\sum_{i\neq j} x_{ij}$	−108.77	−88.49	−11.99	−33.41	−18.49	−13.86
ν_i	2 820.56	2 781.17	1 750.25	1 502.80	1 250.03	1 170.55
$\%w$	6.10	5.19	1.75	2.27	1.80	1.65
CCSD(T)/cc-pVTZ						
F_{ii}	4.764 287	4.931 374	13.034 858	1.691 586	0.830 064	0.264 728
w_i	2 995.85	2 929.23	1 780.76	1 543.21	1 274.88	1 192.20
$2x_{ii}$	−74.01	−63.10	−18.76	−1.85	−4.44	−6.36
$\frac{1}{2}\sum_{i\neq j} x_{ij}$	−108.05	−87.47	−12.70	−33.11	−18.19	−14.23
ν_i	2 813.80	2 778.66	1 749.31	1 508.24	1 252.24	1 171.60
$\%w$	6.08	5.14	1.77	2.27	1.78	1.73

* deperturbed for $2_1 6_1(b_2) \approx 5_1(b_2)$ and $3_1 6_1(b_2) \approx 5_1(b_2)$ or $3_2(a_1) \approx 1_1(a_1)$ Fermi resonance. Structural parameters for the cc-pVXZ (X=T,Q,5) progression are: r_e(CO) = 1.20957, 1.20658, 1.20634 Å; r_e(CH) = 1.10328, 1.10218, 1.10179 Å; and θ_e(HCH) = 116.185, 116.442, 116.597°.

Table 5: $\tilde{X}\ ^1A_1(S_0)$ H_2CO Fundamental Vibrational Frequencies (cm^{-1})

		1 (a_1)	2 (a_1)	3 (a_1)	4 (b_1)	5 (b_2)	6 (b_2)		
Experiment									
Bouwens[a]		2782.2(10)	1746.1(10)	1500.2(10)	1167.4(10)	2843.0(10)	1249.6(10)		
Tchana[b]		2782.4569(10)	1746.00928(49)	1500.1747(4)	1167.2563(4)	2843.3256(10)	1249.0948(3)		
This work	**Method**	***Difference from experiment***[b]						**MAE**	**MAPE**
CCSD(T)/TZ	VPT2	-5.13*	3.30	8.07	4.34	2.27*	3.15	4.38	0.269
CCSD(T)/QZ	VPT2	-2.80*	4.24	2.63	3.29	5.45*	0.94	3.22	0.178
CCSD(T)/5Z	VPT2	-2.00*	1.97	0.28	1.47	6.07*	-0.82	2.10	0.101
CCSDT(Q)/CBS	VPT2	-1.25*	-0.47	-0.24	-0.14	6.71*	-0.14	1.49	0.058
$+\Delta_{\text{rel}}$	VPT2	-1.71*	-1.48	-0.19	-0.34	6.10*	-0.26	1.68	0.119
CCSDT(Q)/CBS	DVR	1.18	-0.32	-0.03	-0.80	1.06	0.03	0.57	0.029
$+\Delta_{\text{rel}}$	DVR	0.49	-1.48	0.01	-0.95	0.25	-0.08	0.54	0.034
Previous Theory									
CCSD(T)/aTZ[c]	VCI	0.94	-11.11	-5.48	-4.76	0.27	-8.49	5.18	0.355
CCSD(T)-F12b/aTZ[c]	VCI	1.74	1.29	-2.48	-0.06	6.07	-3.29	2.49	0.131
CCSD(T)/TZ[d]	VPT2	-5.56	3.89	8.13	4.14	-51.63	3.51	12.81	0.569
CCSD(T)/TZ[d]	VCI	6.74	2.99	4.12	-1.56	-1.33	-1.19	2.99	0.161
Empirical Fit[e]	CVPT	-0.16	0.09	-0.67	0.04	-0.83	-0.19	0.33	0.017
CCSD(T)/aQZ[f]	TROVE	-0.72	-1.40	-1.08	-1.16	-0.96	-3.49	1.47	0.098
Empirical Fit[f]	TROVE	0.00	0.02	0.01	0.04	-0.02	-0.02	0.02	0.001

* treated for the Fermi resonances.

[a] DF spectroscopy results from Ref. 29. [b] Analysis from multiple sources as seen in Refs. 122,123.

[c] Ref. 127. [d] Untreated VPT2 and VSCF-CI "raw" results from Ref. 65.

[e] Empirical fit of Martin et al.'s SPF CCSD(T)/TZ QFF from Ref. 2.

[f] Yachmenev et al.'s variational results from fit of CCSD(T)/aQZ PES in Ref. 5.

Table 6: Comparison of VPT4 H_2CO VBOs (cm^{-1})

Level	Symm.	Exp	ΔExp	DVR(Exact)	ΔVPT2†	VPT2†	ΔVPT4†	VPT4†	ΔVPT4‡	VPT4‡
4_1	b_1	1167.26	-0.80	1166.46	0.23	1166.69	0.05	1166.51	-0.42	1166.08
6_1	b_2	1249.09	0.03	1249.13	-0.27	1248.86	0.03	1249.16	-1.15	1248.01
3_1	a_1	1500.17	-0.03	1500.15	-0.25	1499.90	0.02	1500.17	-1.22	1498.95
2_1	a_1	1746.01	-0.32	1745.69	-0.28	1745.41	0.03	1745.71	-0.15	1745.56
4_2	a_1	2327.52	-3.06	2324.47	3.09	2327.56	0.17	2324.63	0.17	2324.80
4_16_1	a_2	2422.97	-0.32	2422.65	-0.10	2422.55	0.17	2422.82	-2.02	2420.80
6_2	a_1	2494.35	0.52	2494.87	-1.07	2493.81	0.13	2495.00	-2.63	2492.37
3_14_1	b_1	2667.05	-0.17	2666.88	-0.67	2666.21	0.10	2666.98	-2.75	2664.23
3_16_1*	b_2	2719.16	1.32	2720.47	8.88	2729.36	3.77	2724.25	-3.86	2720.39
1_1*	a_1	2782.46	1.18	2783.64	-3.71	2779.93	1.57	2785.21	-2.03	2783.18
5_1*	b_2	2843.33	1.06	2844.39	-66.90	2777.49	260.77	3105.16	-4.16	3101.00
2_14_1	b_1	2905.97	-1.24	2904.73	0.09	2904.82	0.10	2904.83	-0.95	2903.87
2_16_1*	b_2	3000.07	-0.17	2999.90	55.47	3055.37	-264.49	2735.41	0.08	2735.49
2_13_1	a_1	3238.45	-0.15	3238.31	-0.08	3238.16	-0.14	3238.16	-1.52	3236.64
2_2	a_1	3471.6	-0.5	3471.07	0.19	3471.26	0.01	3471.08	-0.13	3470.95
4_3	b_1	3480.7	-6.3	3474.42	8.19	3482.60	-0.90	3473.51	1.47	3474.98

* Fermi resonance affected energy levels. See text for details.

Level assignment from VPT4† results. Experimental results from Refs. 5 and 29.

ΔVPTn† = VPTn† - DVR and ΔVPT4‡ = VPT4‡ - VPT4†.

† V($\mathbf{q}$) LSQ fit from the CCSDT(Q)/CBS PES used in DVR(Exact).

‡ HF/TZ $V_6(\mathbf{q'})$ from a local version of DALTON2013.

Table 7: CCSDT(Q)/CBS VBOs of D_2CO and HDCO (cm^{-1})

	D_2CO			HDCO		
	VPT2	DVR	Exp[a]	VPT2	DVR	Exp[b]
$\nu_1(a_1)$	2063.94*	2061.53	2054.694000(81)	2097.37*	2095.95	2104.4[c]
$\nu_2(a_1)$	1701.27	1701.11	1701.619103(32)	1723.90	1723.83	1724.0
$\nu_3(a_1)$	1099.98	1100.22	1100.44254(74)	1396.18	1396.49	-
$\nu_4(b_1)$	937.75	937.32	938.03549(68)	1058.60	1058.03	1059.6
$\nu_5(b_2)$	2166.47*	2163.15	2162.923385(66)	2854.57*	2845.31	-[d]
$\nu_6(b_2)$	988.86	988.92	989.25028(59)	1027.92	1028.01	1027.1

HDCO (C_s) modes described with H_2CO (C_{2v}) spectroscopic ordering.

[a] FTIR results from Refs 128, 129, and 130.

[b] DF spectra from Ref 131 (˜2 cm^{-1} linewidth in spectra).

[c] Vibrational admixture with a DF spectra assignment of $-4_2 + 1_1 + 6_2$.

[d] Unobserved in the DF spectra; not to be confused with $5_1 + 3_2 = 2846.8$ cm^{-1}.

Values with asteriks treated for resonance interactions with eigenvalues shown below.

$5_1 \approx 3_1 6_1 (b_2)$ eigenvalues are: 2068.15, 2166.47 cm^{-1}.

$4_2, 6_2, 1_1, 3_2 (a_1)$ eigenvalues are: 1864.91, 1972.75, 2063.94, 2201.79 cm^{-1}.

$5_1, 2_1 6_1, 3_2 (a')$ triad eigenvalues are: 2729.43, 2754.03, 2854.57 cm^{-1}.

$1_1, 4_2, 6_2 (a')$ triad eigenvalues are: 2032.29, 2097.37, 2135.51 cm^{-1}.

Table 8: Anharmonicity Constants (cm^{-1})

	This work[a]				**Martin**[b]	**Reisner**[c]	**Bouwens**[c]
x_{ij}	CBS	5Z	QZ	TZ	TZ	Exp.	
11	-32.07	-31.97	-31.93	-31.55	-31.51	-28.95(14)	-50.65(139)
21	-1.78	-1.86	-1.92	-2.27	-2.27	1.15(19)	0.40(92)
22	-9.77	-9.63	-9.60	-9.38	-9.95	-9.926(23)	-10.00(20)
31	-27.16*	-27.08*	-26.96*	-26.06*	-30.05	-23.03(14)	-26.80(137)
32	-7.07	-6.97	-7.08	-7.50	-7.49	-8.26(11)	-8.27(31)
33	-0.75*	-0.66*	-0.72*	-0.93*	0.08	-0.164(97)	-0.55(39)
41	-7.64	-7.56	-7.54	-7.51	-7.44	-10.099(65)	-8.67(81)
42	-7.19	-7.07	-7.10	-7.27	-7.26	-7.199(39)	-7.12(15)
43	-0.34	-0.32	-0.38	-0.79	-0.80	-1.769(52)	-1.59(19)
44	-2.81	-2.80	-2.92	-3.18	-3.41	-3.157(12)	-2.91(8)
51	-133.14	-132.49	-132.25	-131.32	-131.15	-193.32(24)	-88.47(473)
52	-0.70*	-0.85*	-0.97*	-1.54*	-46.62	-17.23(23)	-14.38(334)
53	-34.63*	-34.41*	-34.25*	-33.47*	-10.73	6.00(37)	-5.86(287)
54	-19.84	-19.55	-19.57	-19.63	-19.57	-13.35(17)	-10.26(219)
55	-37.58	-37.29	-37.18	-37.00	-36.95	-17.97(13)	-14.66(245)
61	-8.37	-8.36	-8.31	-7.78	-7.74	-49.78(33)	-15.72(136)
62	-6.78*	-6.90*	-6.91*	-6.81*	38.30	6.581(49)	3.82(186)
63	2.26*	1.99*	1.86*	1.59*	-21.07	-29.861(88)	-33.36(275)
64	7.07	6.79	6.87	6.74	7.09	-2.860(70)	2.40(66)
65	-30.70*	-30.54*	-30.48*	-30.14*	-52.42	-17.63(33)	-7.65(283)
66	-1.94	-2.16	-2.19	-2.22	-2.20	-1.567(56)	-2.35(254)

* computed with resonance denominators removed.

[a] CCSDT(Q)/CBS and CCSD(T)/cc-pVXZ (X=T,Q,5) results.

[b] CCSD(T)/TZ *ab initio* results from Ref. 65.

[c] SEP or DF spectroscopy in Ref. 26 or Ref. 29.

Table 9: CCSDT(Q)/CBS Vibration-Rotation α Constants (MHz)

	A	B	C
α_1	4909.417	11.067	67.110
α_2	89.510	217.061	266.381
α_3	-1894.655	-252.883	78.093
α_4	4300.901*	373.052	-39.664
α_5	2710.134	44.366	43.244
α_6	-3644.134*	-75.243	190.938

* treated for Coriolis resonance.

Table 10: First ($\boldsymbol{D}^5_\omega$) and Second ($\boldsymbol{D}^5_{\omega,\omega'}$) Harmonic Derivatives of $\boldsymbol{\nu_5(b_2)}$

(Q)/CBS*	ν_5	ν_5	ω_5	ω_2	ω_3	ω_6
ω_5	-1.826	ω_5	-0.0869	0.0880	-0.0011	-0.0869
ω_2	1.726	ω_2	0.0880	-0.0880	0.0000	0.0880
ω_3	0.110	ω_3	-0.0011	0.0000	0.0011	-0.0011
ω_6	1.835	ω_6	0.0869	-0.0880	0.0011	0.0869
(T)/5Z	ν_5	ν_5	ω_5	ω_2	ω_3	ω_6
ω_5	-1.484	ω_5	-0.0622	0.0633	-0.0011	0.0622
ω_2	1.382	ω_2	0.0633	-0.0633	0.0000	-0.0633
ω_3	0.112	ω_3	-0.0011	0.0000	0.0011	0.0011
ω_6	1.493	ω_6	0.0622	-0.0633	0.0011	-0.0622
(T)/QZ	ν_5	ν_5	ω_5	ω_2	ω_3	ω_6
ω_5	-1.135	ω_5	-0.0395	0.0407	-0.0012	0.0395
ω_2	1.028	ω_2	0.0407	-0.0407	0.0000	-0.0407
ω_3	0.117	ω_3	-0.0012	0.0000	0.0012	0.0012
ω_6	1.144	ω_6	0.0395	-0.0407	0.0012	-0.0395
(T)/TZ	ν_5	ν_5	ω_5	ω_2	ω_3	ω_6
ω_5	-0.873	ω_5	-0.0238	0.0252	-0.0014	-0.0238
ω_2	0.752	ω_2	0.0252	-0.0252	0.0000	-0.0252
ω_3	0.131	ω_3	-0.0014	0.0000	0.0014	0.0014
ω_6	0.882	ω_6	0.0238	-0.0252	0.0014	-0.0238

Unitless and cm for first and second derivatives, respectively.

*CCSDT(Q)/CBS results, see Eqn. 3.

Table 11: Effects of the 5_1, 2_16_1, 3_16_1 (b_2) Resonance Triad on $\nu_5(b_2)$ (cm^{-1})

	$\boldsymbol{\Delta\omega}$			$\boldsymbol{\nu_5(b_2)}$			**Contribution**	
Theory	$5_1 \approx 2_16_1$	$5_1 \approx 3_16_1$	Deperturbed	K=0	Full K	5_1	2_16_1	3_16_1
CCSD(T)/TZ	-59.79	177.77	2813.80	2844.70	2845.60	0.586	0.065	0.349
CCSD(T)/QZ	-50.65	193.16	2820.56	2847.99	2848.78	0.621	0.073	0.306
CCSD(T)/5Z	-43.72	200.17	2822.93	2848.62	2849.40	0.631	0.080	0.290
CCSDT(Q)/CBS	-39.29	202.63	2823.98	2849.35	2850.04	0.628	0.083	0.289
				Spectroscopic Constants				
Theory	$\frac{1}{\sqrt{8}}\phi_{652}$	$\frac{1}{\sqrt{8}}\phi_{653}$	K	x_{52}	x_{53}	x_{62}	x_{63}	x_{65}
CCSD(T)/TZ	51.921	63.546	-2.932	-1.54 (-47)	-33.47 (-11)	-6.81 (38)	1.59 (-21)	-30.14 (-53)
CCSD(T)/QZ	51.410	65.231	-2.621	-0.97 (-53)	-34.25 (-12)	-6.91 (45)	1.86 (-20)	-30.48 (-61)
CCSD(T)/5Z	51.435	65.998	-2.527	-0.85 (-61)	-34.41 (-13)	-6.90 (54)	1.99 (-20)	-30.54 (-69)
CCSDT(Q)/CBS	51.651	66.225	-2.205	-0.70 (-69)	-34.63 (-13)	-6.78 (61)	2.26 (-19)	-30.70 (-77)

$\nu_2(a_1) + \nu_6(b_2) \approx \nu_5(b_2)$ and $\nu_3(a_1) + \nu_6(b_2) \approx \nu_5(b_2)$ related denominators removed.

Values in parentheses correspond to x_{ij} without removal of resonance denominators.

K=0 and Full K values correspond to the ν_5 eigenvalue of $\mathbf{H_{eff}}$ in Eqn. 11.

Table 12: Quartic and Sextic Centrifugal Distortion Constants (in MHz) from the S and A Reductions

Parameter	Experiment^a		This work	Parameter	Experiment^a	This Work	Martin^b	Carter^c
D_J $\times 10^3$	70.321 00(68)	70.320 5(50)	70.254 96	$\mathit{\Delta}_J$ $\times 10^3$	75.322 46(75)	74.566 94	72.730	76.807 3
D_{JK} $\times 10^3$	1 321.101(15)	1 321.107 3(93)	1 319.308	$\mathit{\Delta}_{JK}$ $\times 10^3$	1 291.220(23)	1 293.436	1 265.2	1 275.365
D_K $\times 10^3$	19.390 89(72)	19.39 136(53)	18.617 20	$\mathit{\Delta}_K$ $\times 10^3$	19.415 83(73)	18.638 76	18.609	18.113 38
d_1 $\times 10^3$	−10.437 98(18)	−10.437 877(47)	−9.903 52	δ_J $\times 10^3$	10.454 11(21)	9.903 52	9.563	10.960 4
d_2	−2.501 461(58)	−2.501 496(33)	−2.155 991	δ_K	1.028 291(34)	0.917 961	0.896	-
H_J $\times 10^9$	3.92(47)	3.54(33)	3.40	$\mathit{\Phi}_J$ $\times 10^9$	97.45(53)	85.09	89.94	-
H_{JK} $\times 10^6$	7.453(31)	7.465(16)	7.403	$\mathit{\Phi}_{JK}$ $\times 10^6$	32.802(60)	26.815	25.812	-
H_{KJ} $\times 10^6$	10.72(16)	10.865(79)	12.66	$\mathit{\Phi}_{KJ}$ $\times 10^6$	−74.10(43)	−53.28	−58.19	-
H_K $\times 10^3$	4.021(25)	4.027(22)	3.759	$\mathit{\Phi}_K$ $\times 10^3$	4.077(25)	3.805	3.789	3.428
h_1 $\times 10^9$	32.33(14)	32.272(58)	29.59	ϕ_J $\times 10^9$	48.04(18)	41.27	29.98	-
h_2 $\times 10^6$	47.87(13)	47.942(74)	40.84	ϕ_{JK} $\times 10^6$	16.26(44)	14.33	13.76	-
h_3 $\times 10^3$	15.946(31)	15.966(15)	11.686	ϕ_K $\times 10^3$	1.543 2(31)	1.189 6	1.156 0	-

[a] Terahertz spectroscopy results from Ref. 30 with revised results from Ref. 132.

[b] CCSD(T)/TZ QFF results from Ref. 65.

[c] Empirically fit PES from Ref. 133.

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