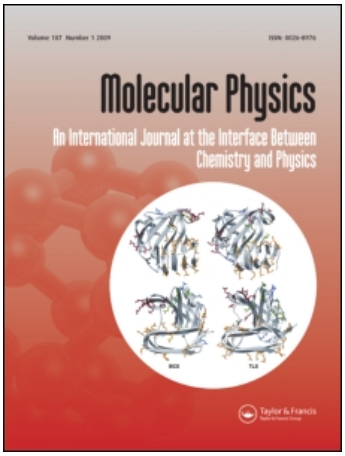

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INVITED ARTICLE

Anharmonic vibrational frequencies and vibrationally-averaged structures of key species in hydrocarbon combustion: HCO^+, HCO, HNO, HOO, HOO^-, CH_3^+, and CH_3†

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A general scheme to predict anharmonic vibrational frequencies and vibrationally-averaged structures and rotational constants of molecules is presented with applications to some key species in hydrocarbon combustion (some also of importance in atmospheric and/or interstellar chemistry): HCO^+, HCO, HNO, HOO, HOO^-,CH_3^+, and CH_3. A combination of coupled-cluster singles and doubles (CCSD), CCSD with a second-order perturbation correction in the space of triples [CCSD(2)$_T$] and in the space of triples and quadruples [CCSD(2)$_{TQ}$], and a correlation-consistent basis set series has been employed to achieve the complete-correlation, complete-basis-set limits of the potential energy surfaces (PESs) of these species near equilibrium geometries. A new, compact representation of PESs that combines two existing representations, namely, a fourth-order Taylor expansion and numerical values on a rectilinear grid, has been proposed and shown to yield accurate frequencies, when combined with vibrational general-order configuration-interaction method. The predicted frequencies (and the observed in parentheses, when available) of the fundamentals are as follows: 823 (830), 2175 (2184), and 3083 (3089) cm^{-1} in HCO^+; 1079 (1081), 1874 (1868), 2432 (2434) cm^{-1} in HCO; 1503 (1501), 1572 (1565), and 2683 (2684) cm^{-1} in HNO; 1121 (1098), 1399 (1392), and 3447 (3436) cm^{-1} in HOO; 739, 1088, and 3587 cm^{-1} in HOO^-; 1383 (1359 ± 7), 1384 (1370 ± 7), 2940, and 3096 (3108) cm^{-1} in CH_3^+; 565 (606), 1377, 3002 (3004), and 3139 (3161) cm^{-1} in CH_3. The mean absolute deviation in the predicted frequencies is 11 cm^{-1}.

Keywords: molecular vibrations; anharmonicity; potential energy surfaces; electron correlation; hydrocarbon combustion

1. Introduction

Schaefer's computational determination of the structures of CH_2 (see his captivating review [1] on this topic) marked the arrival of predictive chemical computing [2] based on converging electron-correlation methods. Combined with systematic basis sets such as the ones developed by Dunning and co-workers [3,4], they can now routinely predict the electronic properties of small but general polyatomic molecules within controlled accuracy. The objective of this study as well as several recent ones in our group [5–7] is to extend the domain of predictive computing to bound nuclear motions, i.e. anharmonic molecular vibrations, vibrationally-averaged properties, and various molecular spectra. In addition to providing computed properties and spectra that can be directly compared with the observed, they can serve as an independent and reliable source of chemical information of which direct experimental measurements may be technically difficult, expensive, and/or dangerous.

The predictive vibrational analyses consist in (1) converging electronic structure methods for generating accurate potential energy surfaces (PESs), (2) compact and systematic representations of the PESs, and (3) hierarchical vibrational many-body methods that can include vibrational anharmonicity and anharmonic mode-mode coupling to any desired extent. For (1), we employ the converging series of combined coupled-cluster (CC) and perturbation theories, i.e. coupled-cluster singles and doubles (CCSD) [8,9], CCSD with a second-order triples correction abbreviated as CCSD(2)$_T$ [10], and CCSD with a second-order triples and quadruples correction or CCSD(2)$_{TQ}$ [10] in this work. For stable molecules near their equilibrium geometries, this is perhaps among the most rapidly converging series of electron-correlation methods.

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†Dedicated to Professor Henry F. Schaefer III on the occasion of his 65th birthday.

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The complete-basis-set (CBS) limits are reached by extrapolation with the correlation-consistent basis sets [11], although an effort to eliminate this step with the aid of the so-called R12 or F12 methods [12] is underway in our group [13–15].

For (2), we propose a new hybrid representation of PESs, which combines a Taylor expansion truncated at the fourth order (a quartic force field or QFF) and numerical energy values on a rectilinear quadrature grid (a grid PES) both in the so-called *n*MR (*n*-mode representation) approximation [16,17]. The QFFs are among the most accurate and compact PES representations for low-lying vibrational states [18–25]. However, they cannot describe strong Morse-like anharmonicity and tend to exhibit fortuitous minima in the regions away from the equilibrium geometries [26,27]. When the general-order vibrational configuration-interaction method (VCI) is applied to these QFFs, errors (with respect to grid PESs) in the frequencies of stretching modes involving hydrogen motions can be as large as $20\,cm^{-1}$ (see below) and nonphysical states supported by the fortuitous minima can appear. Such nonphysical states can be easily identified by an inspection of wave functions or, alternatively, a Morse-like [28] or similar coordinate transformations [26] can be applied before the VCI step to avoid both problems. In this study, however, we circumvent them by improving the global representation of a PES qualitatively by combining a QFF and a grid PES [18,29,30] while further improving the local representation near the equilibrium geometry quantitatively. Grid PESs maintain an equal accuracy (subject to errors in electronic structure methods used) in the entire geometry domain covered by the grids, but they are exponentially expensive to compute (without *n*MR approximation) as the number of atoms increases. The new hybrid representation combines a QFF obtained by high-rank electronic structure methods in the CBS limits and a grid PES obtained by low-rank methods and smaller basis sets. The proposed hybrid QFF/grid PESs are expected to be most meritorious when applied to large-amplitude motions and highly excited vibrational states. The QFFs, grid PESs, and hybrid QFF/grid PESs are defined in normal coordinates [31]. Although local coordinates may be more suitable for large-amplitude motions or highly excited vibrational states, we adopt normal coordinates for their unambiguousness, convenience, and generality [27,32].

Vibrational many-body problems in these PESs are solved by vibrational self-consistent-field (VSCF) [33–36], second-order Møller–Plesset perturbation (VMP2) [16,29,37,38], and VCI [39] methods implemented in the SINDO program developed by one of the authors [40]. See a recent review [27] for the details of these methods as well as the vibrational coupled-cluster methods (VCC) [41] added recently to the repertory of vibrational many-body methods. Although this method is not used in this study, it is a promising method for its size-extensivity which makes it the right tool for larger systems where a full VCI is not applicable. The necessary molecular integrals are computed over the harmonic oscillator basis functions along the normal coordinates. Together, our composite vibrational method can attain complete-correlation, CBS (CC-CBS) limits in anharmonic frequencies and vibrationally-averaged properties in a cost-effective fashion (although its applicability to large molecules is still limited).

We apply the method to seven key species in hydrocarbon combustion: the formyl cation (HCO^+), the formyl radical (HCO), the nitrosyl hydride (HNO), the hydroperoxy radical (HOO), the hydroperoxy anion (HOO^-), the methyl cation (CH_3^+), and the methyl radical (CH_3). Some are important in atmospheric and/or interstellar chemistry also. There is a considerable lack of experimental data of molecular constants of these species, since most of them are unstable under typical laboratory conditions and, therefore, their characterization calls for a predictive theory. For instance, the transition frequencies of one of the fundamentals of CH_3 and CH_3^+ as well as all of the fundamentals of HOO^- are unknown, in spite of the significance of these species and their vibrational spectra as a source of information about hydrocarbon combustion processes. Furthermore, the comparison of predicted frequencies and rotational constants with the observed values, when available, serves as a rigorous test of the validity and accuracy of the computational scheme, including the hybrid QFF/grid PESs proposed in this work.

There has been a considerable body of work [21–25,42–44] reporting high accuracy anharmonic frequencies of fundamental vibrations of small molecules. Some of these works are based on QFF in tailored coordinates, vibrational perturbation theories including Coriolis coupling, and various CBS extrapolations of electronic energies, including small electronic effects such as core correlation and relativistic effects as well as diagonal Born–Oppenheimer corrections. In contrast to these previous high-accuracy studies, this study and a few previous ones [5–7] from our group aim at establishing blackbox computational procedures for low-lying anharmonic vibrational frequency calculations applicable generally and unambiguously to various polyatomic molecules in the same sense of 'model chemistry' advocated by Pople (see, e.g., [45]) in electronic structure theory. The reliance on

normal modes, the mixed use of QFF, grid, and hybrid QFF/grid PES representations, and the open-ended combinations of systematic electronic and vibrational many-body methods in this work are to achieve good balance between general applicability of the theories, robustness and availability of the implementations, and high (if not the highest) accuracy. A wider range of molecules (seven species) that are studied in one place is also to show the generality of our model chemistry, its uniform accuracy, and affordability of computations both in terms of computational cost and the ease of use for non-experts of computational chemistry.

It will be shown that the hybrid PESs constitute a uniform and inexpensive improvement over both QFFs and grid PESs. When combined with the CC-CBS electronic structure method and VCI, it reproduces the frequencies of the fundamentals within the mean absolute deviation of $11\,\mathrm{cm}^{-1}$ and the maximum deviation of $41\,\mathrm{cm}^{-1}$. Our calculated results are reliable predictions (within ca $20\,\mathrm{cm}^{-1}$) for the hitherto-undetermined fundamental frequencies of HOO^-, CH_3^+, and CH_3. The predicted rotational constants also serve as an additional basis for correct band assignments, although in some instances they are found to be unreliable because of strong centrifugal distortion and Coriolis coupling, which are neglected in this work. The vibrationally-averaged structural parameters are expected to be accurate to within several thousandths of 1 Å and are possibly more accurate than experimentally derived values. While our computational scheme is still severely limited in its applicability to large molecules, it is a general, predictive, blackbox method applicable to any polyatomic molecule.

2. Theory and computational procedure

2.1. *Electronic part*

Geometry optimization and normal coordinate calculations were performed with CCSD(2)$_T$ with the aug-cc-pVDZ basis set. All PESs of a molecule were represented in this single set of coordinates to facilitate the CC-CBS extrapolation. Three different CBS extrapolation schemes (Equations (1)–(3)) were examined on the basis of the CCSD energies obtained with the aug-cc-pVXZ basis sets in the range of X = D, T, and Q (abbreviated hereafter as 'aXZ'). The first of these is the exponential-Gaussian three-point extrapolation formula advocated by Peterson, Woon, and Dunning [46], which assumes the energy obtained with the lth basis set ($l = 2$, 3, and 4 correspond to X = D, T, and Q, respectively) satisfy the following equation,

$$E(l) = E_{\mathrm{CBS}} + A\exp[-(l-1)] + B\exp\left[-(l-1)^2\right] \quad (1)$$

where A, B, and E_{CBS} are constants (the last quantity corresponds to the CBS total energy). The second is the power law three-point formula proposed by Martin and Lee [47], which can be written as

$$E(l) = E_{\mathrm{CBS}} + A(l+1/2)^{-4} + B(l+1/2)^{-6}, \quad (2)$$

where the meaning of the variable l and the constants are the same as in Equation (1). The third is the two-point formula of Helgaker *et al*. [48]:

$$\Delta E(l) = \Delta E_{\mathrm{CBS}} + Al^{-3} \quad (3)$$

where $\Delta E(l)$ and ΔE_{CBS} represent the correlation energy of the lth basis set (with $l = 3$ and 4) and at the CBS limit, respectively. The CBS correlation energies obtained with the third extrapolation formula was combined with the Hartree–Fock (HF) energies in the CBS limit obtained by Equation (1) or (2). Table 1 shows that there is no significant difference in anharmonic vibrational frequencies among these formulas for the purpose of this paper. This result also indicates the robustness of our final predictions with respect to the arbitrary choice of empirical extrapolation formulas. We elected to use Equation (1) for the rest of the calculations without assuming any superiority of this formula over the others. The CC-CBS limits ($E_{\text{CC-CBS}}$) were obtained by the following formula [49]:

$$E_{\text{CC-CBS}} = \left(E_{\mathrm{CCSD/CBS}} - E_{\mathrm{CCSD/aDZ}}\right) \times \frac{E_{\mathrm{CCSD(2)}_T\mathrm{/aTZ}} - E_{\mathrm{CCSD(2)}_T\mathrm{/aDZ}}}{E_{\mathrm{CCSD/aTZ}} - E_{\mathrm{CCSD/aDZ}}} + E_{\mathrm{CCSD(2)}_{TQ}\mathrm{/aDZ}}. \quad (4)$$

This procedure will not yield the absolute energies accurately but is expected to minimize the errors in the energy differences, i.e. the shape of the PESs. To obtain a CC-CBS energy, one must execute only three single-point energy calculations at the CCSD/aQZ, CCSD(2)$_T$/aTZ, and CCSD(2)$_{TQ}$/aDZ levels.

Table 1. Comparison of the fundamental vibrational transitions energies (in cm^{-1}) of HNO obtained with different CBS extrapolations. Correlation energy (ΔE) is obtained by CCSD method and aXZ basis sets are used where X = D, T, and Q.

HF CBS	ΔE CBS	(100)[a]	(010)[a]	(001)[a]
Equation (1)	Equation (1)	1542.5	1655.6	2760.8
Equation (2)	Equation (2)	1543.5	1658.8	2760.9
Equation (1)	Equation (3)[b]	1543.2	1657.0	2763.3
Equation (2)	Equation (3)[b]	1543.5	1658.5	2763.2

[a]The vibrational quanta of the N–H stretch, bend, and N–O stretch, respectively.
[b]The aTZ and aQZ basis sets are used.

The CCSD/aTZ energy is obtained as a byproduct of the CCSD(2)$_T$/aTZ calculation and the CCSD/aDZ and CCSD(2)$_T$/aDZ energies from CCSD(2)$_{TQ}$/aDZ. These were carried out within the frozen core approximation using the NWChem [50] and ACES II [51] programs.

2.2. *Potential energy surfaces*

In his two seminal works [52,53], Watson rearranged the normal coordinate nuclear Hamiltonian in a simpler form. For nonlinear reference configurations, the vibration-only part of this Hamiltonian is

$$\hat{H} = -\frac{1}{2}\sum_{i=1}^{m}\frac{\partial^2}{\partial Q_i^2} + \hat{V}(Q_1,\ldots,Q_m) + \frac{1}{2}\sum_{\alpha\beta}\hat{\pi}_\alpha\mu_{\alpha\beta}\hat{\pi}_\beta - \frac{1}{8}\sum_{\alpha}\mu_{\alpha\alpha}, \quad (5)$$

where Q_i is ith normal coordinate, m is the total vibrational degrees of freedom, and $\hat{V}$ represents the Born–Oppenheimer PES. The last two terms involve $\mu_{\alpha\beta}$ which is the generalized inverse inertia tensor and $\hat{\pi}_\alpha$ in the third term, the so-called vibrational angular momenta operator, arises owing to Coriolis coupling. These terms cause singularities in the Watson Hamiltonian for linear geometries, thereby greatly complicating a robust computer implementation. A very detailed study [54] on the significance of the last two terms shows that the last term is rather important for the zero-point vibrational energy (ZPVE), but it does not alter the transition energies significantly in contrast to the third term which has more influence on the latter. In principle, these terms become more important for the molecules that have large rotational constants (small moments of inertia) like the water molecule. Studies on the water molecule [54–56] show that although the errors (relative to the Watson Hamiltonian results) can be severe for high-lying vibrational states, they are only around 10 cm^{-1} for the fundamentals. While an implementation of the Watson Hamiltonian is mandatory for spectroscopic accuracy (<1 cm^{-1}) and successful applications for small molecules exist in the literature [44], we neglect the last two terms in Equation (4) which is justifiable for the target accuracy of a few 10 cm^{-1} for general polyatomic molecules. This is consistent with our neglect of core-correlation corrections, relativistic effects, non-Born–Oppenheimer effects, higher-order correlation effects, etc. The Hamiltonian used in this work, therefore, reads

$$\hat{H} = -\frac{1}{2}\sum_{i=1}^{m}\frac{\partial^2}{\partial Q_i^2} + \hat{V}(Q_1,\ldots,Q_m) \quad (6)$$

for both linear and nonlinear molecules without any forms of singularity. However, as we shall show in the following, the approximate Hamiltonian used in this study is likely responsible for some pronounced errors in predicted vibrationally averaged rotational constants.

For the PES, we adopted the nMR approximation [16,17] that expressed $\hat{V}$ as a sum of one-, two-, up to m-mode coupling terms and truncated the sum after the n-mode coupling terms. We used $n=3$ or the 3MR approximation, which amounted to a non-truncated PES for nonlinear triatomic molecules. We defined a rectilinear grid along the CCSD(2)$_T$/aDZ normal coordinates centered at the CCSD(2)$_T$/aDZ optimized geometry. Eleven grid points were placed along each normal coordinate according to the Gauss–Hermite quadrature rule and single-point electronic structure calculations were performed on the geometries of these points. In the 3MR approximation, there were $\binom{m}{3}11^3$ grid points in total, if we disregard symmetry advantages. This number has been shown to be sufficient [18] for several low-lying vibrational states of the molecules studied here. Grid-based algorithms for anharmonic vibrational problems are quite old [57,58], but they became routine [18,29,30] only after they were combined with the nMR approximation. An inexpensive alternative is the QFFs, which are computed by a finite difference method described in [19,20], requiring only a few tens of single-point energy calculations to compute. We used both representations in this work with SINDO that took advantage of the Abelian sub-group of the symmetry group of a molecule. While highly accurate near the equilibrium geometries, the QFFs become progressively unrealistic as the geometries are more distorted. They also cannot dissociate bonds and often deflect downwards away from the equilibrium geometries, often causing artificial minima in a PES. The grid PESs do not share these shortcomings, but they are exponentially expensive to compute. Here, we propose a new hybrid representation, which combines the merits of the grid and QFF representations, while keeping the overall computational cost manageable. It involves a grid and QFF obtained at the same low electronic structure level and another QFF at a higher electronic structure level and adds the difference between high- and low-level QFFs to the low-level grid PESs:

$$E_{\text{hybrid}} = E_{\text{QFF/high}} - E_{\text{QFF/low}} + E_{\text{grid/low}}, \quad (7)$$

where $E_{\text{QFF/high}}$ and $E_{\text{QFF/low}}$ are the energies at a given grid point obtained by evaluating the quartic polynomial functions of high- and low-level QFFs,

Table 2. Comparison of the three fundamental vibrational transitions energies (in cm^{-1}) of HOO^- obtained with three PES representations (QFF, grid, and hybrid QFF/grid) and the full VCI. Except for the grid CCSD(2)$_T$/aTZ results (the top row), which serve as the accurate reference frequencies, the differences from the reference values are shown.

PES	(100)[a]	(010)[a]	(001)[a]
CCSD(2)$_T$/aTZ (grid)	3572.2	1082.2	747.7
Hybrid QFF/grid[b]	+3.1	+0.5	+0.2
CCSD(2)$_T$/aTZ (QFF)	−21.5	+1.2	−11.6
CCSD/aDZ (grid)	+2.0	+17.4	+0.3
CCSD/aDZ (QFF)	−19.3	+24.6	−5.0

[a]The vibrational quanta of the O–H stretch, bend, and O–O stretch, respectively.
[b]Combines the PESs in the last three rows.

respectively, and $E_{grid/low}$ is the energy value directly computed at the grid point at the low-level method. The left-hand side is the hybrid QFF/grid PES defined numerically on the same grid and approximates the grid PES obtained at the high-level method.

The remarkable performance of this hybrid representation can be seen in Table 2 in which anharmonic vibrational frequencies of HOO^- obtained with five different PESs are compared. Relative to the grid PES obtained by CCSD(2)$_T$/aTZ, which serves as the accurate and very expensive reference, the two PESs obtained by CCSD/aDZ suffer from large errors in excess of 30 cm^{-1} in the vibrational energies. These are clearly due to the inherent errors in the CCSD/aDZ regardless of the representation (grid or QFF). If we raise the electronic structure level to CCSD(2)$_T$/aTZ (the same as the reference), however, the QFF representation is still responsible for an error of –22 cm^{-1} in the O–H stretching frequency. When these three PESs (the bottom three rows) are combined and the hybrid QFF/grid PES is formed, the errors become uniformly small (within 3.1 cm^{-1}). They are much smaller than those obtained with any of the three constituent PESs. Note also that forming the hybrid PES is an order of magnitude less expensive than generating the corresponding grid PES and, furthermore, the advantage of the former is expected to grow as molecules become larger. We adopted the hybrid representation for all the molecules studied here. We chose CCSD/aDZ as the low electronic structure level to obtain the grid PES and the CC-CBS composite defined by Equation (4) for the QFFs. Four PES scans (three QFF calculations for CC-CBS and one grid PES calculation for forming the hybrid PES) were run for each molecule, apart from the geometry optimization and normal coordinate determination.

2.3. *Vibrational part*

With the accurate PESs thus obtained, we solved the vibrational Schrödinger equation with the VSCF, VMP2 and VCI methods (the VSCF and VMP2 results are not shown), using SINDO. The full VCI method was applied to the nonlinear and linear triatomic molecules (involving 1331 and 14641 VSCF configurations, respectively). For tetratomic molecules, we examined two configuration selection schemes. In one, all VSCF configurations that involved simultaneous excitations of up to three modals (21561 configurations) were included. In the other, simultaneous excitations of up to four modals were allowed but the sum of vibrational quanta was limited to 15. There were 30011 VSCF configurations in the latter. It was confirmed that the fundamental frequencies obtained in either of these schemes were converged within 1 cm^{-1} of the limits with respect to the configuration space size. The vibrationally-averaged structural parameters (at zero temperature) were obtained by using the VCI wave functions. The expectation values of the relative nuclear positions in the normal mode coordinates were calculated and then they were transformed into the Cartesian coordinates. The vibrationally-averaged rotational constants were computed by evaluating the rigid-rotor formulae of the rotational constants with the vibrationally-averaged nuclear coordinates. Note that there are at least two approximations in this treatment. First, they do not correspond to the expectation values that are observed as rotational constants. Second, they neglect rovibrational coupling such as centrifugal distortion and Coriolis coupling. As a result, the computed rotational constants can deviate, sometimes significantly, from experimental values and are at best of a semi-quantitative value.

3. Combustion chemistry applications

3.1. *HCO^+ ($\tilde{X}^1\Sigma^+$)*

The formyl cation (HCO^+) in its $\tilde{X}^1\Sigma^+$ state is a linear molecule ubiquitous in interstellar medium [59] and also in hydrocarbon flames [60]. Buhl and Snyder [61] observed an interstellar transition which was identified computationally by Klemperer [62] as a rotational transition of HCO^+. Klemperer's computational assignment was supported theoretically [63] and subsequently confirmed experimentally [64]. Its rotational and vibrational transitions have been thoroughly characterized by microwave [65–73] and infrared laser spectroscopy [74–83]. There have been many computational studies on the structure, PES [84–89], and rovibrational spectra [90–93] of HCO^+.

Some [90,92,93] are based on CCSD with noniterative triples [CCSD(T)] while [91] on the multireference configuration interaction (MRCI) and their results on anharmonic vibrational frequencies agree with one another, attesting to the limited multireference character of the wave function of HCO^+.

Table 3 compiles the experimental frequency of the fundamental transitions and four of the most accurate computed frequencies by other groups as well as our computed frequencies. Mladenović and Schmatz [92] computed energies at 842 geometries with CCSD(T)/cc-pVQZ and obtained anharmonic fundamental frequencies by a variational method. They are within $5\,cm^{-1}$ of the observed. The authors state the fitting of the PES by analytical functions has an inherent error of $9\,cm^{-1}$ (the standard deviation), but the error may be mostly due to geometries with high energies and it is possible that the fundamental frequencies can have higher accuracy than the fitting error. However, the result obtained by van Mourik, Dunning, and Peterson [93] using CCSD(T) and a larger basis set (aug-cc-pVQZ) has slightly greater errors, suggesting that the accurate agreement of Mladenović and Schmatz is likely due to some error cancellation between residual basis set effects and other small electronic effects neglected in their work.

Table 3. Fundamental vibrational transition energies (in cm^{-1}) of HCO^+. The frequencies obtained with each of the seven PESs underlying the hybrid PES are given in Table S-1 of the supplementary online material.

Method	$(10^00)^a$	$(01^10)^a$	$(00^01)^a$
Experiment	3088.74[b]	829.72[c]	2183.95[d]
CC-CBS/hybrid/VCI[e]	3083	823	2175
CC-CBS/QFF/VCI[e]	3072	806	2176
$CCSD(2)_T$/aDZ/harmonic[e]	3214	837	2160
Mladenović and Schmatz [92]	3086	831	2179
Puzzarini *et al.* [91]	3090[f]	831[f]	2183[f]
Martin, Taylor and Lee [90]	3088	824	2166
van Mourik, Dunning, and Peterson [93]	3083	823	2177

[a]The vibrational quanta of the C–H stretch, bend, and C–O stretch, respectively.
[b]Amano [75].
[c]Davies and Rothwell [77].
[d]Foster, McKellar, and Sears [78].
[e]This work. The CC-CBS results are based on the CCSD/(aDZ, aTZ, aQZ), $CCSD(2)_T$/(aDZ, aTZ) and $CCSD(2)_{TQ}$/aDZ energies.
[f]The PES was scaled empirically.

Puzzarini *et al.* [91] used MRCI/cc-pVQZ to obtain a sextic force field, and evaluated spectroscopic parameters by second-order perturbation theory. They also scaled this force field empirically and used variational methods to solve for rovibrational energy levels, which yielded the fundamental frequencies within $2\,cm^{-1}$ of the experimental values. An earlier work of Martin, Taylor and Lee [90] was based on CCSD(T)/cc-pVTZ QFF and, because of the smallness of the basis set, had slightly greater errors.

The harmonic frequencies obtained at the $CCSD(2)_T$/aDZ level, which serve as the basis of our subsequent anharmonic calculations, indicate small anharmonicity in the ν_2 (bend) and ν_3 (C–O stretch). The CC-CBS extrapolation of the PES in the QFF representation and a full VCI calculation indeed increases the error in the ν_2 frequency from 7 to $24\,cm^{-1}$, while they bring the computed frequency of ν_1 (C–H stretch) in much better accord with experiment (3072 and $3089\,cm^{-1}$, respectively). This error in the ν_2 frequency is largely due to the QFF and can be removed effectively by switching to the hybrid QFF/grid PES. With the latter, the VCI method places the fundamental frequencies at 3083, 823, and $2175\,cm^{-1}$, which agree with the corresponding experimental values (3089, 830, and $2184\,cm^{-1}$) within $9\,cm^{-1}$. While similar or more accurate agreement has been reported by the previous studies, we note that our proposed method is a black-box approach applicable to general polyatomic molecules with minimum molecule-specific adjustments of coordinates, PES representations, etc. Accuracy higher than this ($9\,cm^{-1}$) cannot be expected without a CC-CBS extrapolation and inclusion of rovibrational couplings, non-Born–Oppenheimer effects, and small electronic effects such as core correlation and relativistic effects [43,44]. The frequencies obtained by the individual methods that lead to the CC-CBS limit (see Section 2.1) are listed in Table S-1. These results reveal that the error arising from basis set truncation and that from the higher-order excitations tend to have opposite signs. Similar pattern was observed for all the molecules studied here. The success of the previous results [90,92,93], therefore, may be partly because of the cancellation of the errors between them, especially for the C–O stretching mode due to its slower convergence in both limits.

Table 4 compares the vibrationally-averaged rotational constants (Bs) with the observed [67,75–77] for four low-lying states. While the absolute values of the calculated constants have errors on the order of 1%, their variation with vibrational states is remarkably accurately reproduced by our scheme. Note that the harmonic approximation is incapable of describing such variation. These computed state-specific

Table 4. Vibrationally-averaged bond lengths (in Å) and rotational constant (B) (in cm^{-1}) of HCO^+ computed by the CC-CBS/hybrid/VCI method (experimental values, when available, in parentheses).

State[a]	(00^00)[a]	(10^00)[a]	(01^10)[a]	(00^01)[a]
r_{C-O}[b]	1.112	1.113	1.112	1.118
r_{C-H}[b]	1.096	1.127	1.081	1.099
B	1.48 (1.49[c])	1.46 (1.48[d])	1.49 (1.49[e])	1.46 (1.48[f])

[a]See footnote a of Table 3.
[b]The equilibrium bond lengths are 1.10474 (r_{C-O}) and 1.09725 Å (r_{C-H}) according to Woods [70].
[c]Sastry, Herbst, and de Lucia [67].
[d]Amano [75].
[e]Davies and Rothwell [77].
[f]Davies, Hamilton, and Rothwell [76].

rotational constants can, therefore, serve as a useful, independent source of information for correct band assignments, when the assignments based on calculated and observed frequencies alone are inconclusive (which is, however, not the case with HCO^+). The potential curves along the C–H and C–O stretches are Morse-like and the corresponding vibrations increase the average C–H and C–O bond lengths, respectively. They result in noticeable reductions in the rotational constants in the (10^00) and (00^01) states. The bending vibration in the linear molecule, in contrast, has a net effect of pulling the terminal H and O atoms closer, causing the rotational constant in the (01^10) state to be slightly greater than the zero-point value. Judging from the computed and observed rotational constants, the predicted C–O and C–H bond lengths should be within several thousandths of 1 Å of the experimental values (unknown).

3.2. *HCO ($\tilde{X}^2A'$)*

Unlike its cationic counterpart, the formyl radical (HCO) in its $\tilde{X}^2A'$ state is bent. The radical was first identified in ethylene flame [94] and was found to be responsible for the blue emission bands known as the hydrocarbon flame bands. It is also an intermediate in the formation of HCO^+ in hydrocarbon flames. A characterization of the radical was performed by electronic absorption spectroscopy during the flash photolysis of acetaldehyde and other aldehydes, identifying two additional absorption bands as the transitions from the ground state in the bent structure to excited states in linear configurations [95,96]. The vibrational frequencies for C–H stretching [97–101], bending [96,101–105] and C–O stretching [100,105–107] of HCO were measured by several experimental groups.

There is a considerable amount of computational studies on the PES of HCO [93,108–130], a significant proportion of which concerns with its anharmonic vibrations. Bowman, Bittman, and Harding [111] reported its PES obtained with the configuration-interaction singles and doubles (CISD) and a double-ζ basis set plus some empirical corrections. This PES (called BBH potential) was modified and used in many subsequent dynamics calculations [114–116,120, 122,125]. Werner *et al.* [123] employed MRCI with a quadruple-ζ basis set and obtained the fundamental anharmonic frequencies that agreed with the experimental values accurately except for the ν_3 (C–O stretch), which was 24 cm^{-1} too low. Serrano-Andrés, Forsberg, and Malmqvist [127] obtained similar results using a 177-point PES obtained with the multireference second-order perturbation method (CASPT2). The CCSD(T)/aQZ work of van Mourik, Dunning, and Peterson [93], in contrast, obtained quantitative agreement between the computed and observed ν_2 (bend) and ν_3 (C–O stretch) frequencies, but the predicted ν_1 (C–H stretch) frequency was too high by 26 cm^{-1}. Marenich and Boggs [129] performed all-electron CCSD(T) calculations in the CBS limits and observed similar overestimation of the ν_1 frequency, causing them to question the experiments. However, the same authors [130] subsequently improved their calculations by including fifth- and sixth-order force constants along the C–H stretch (133 single-point calculations in total) and obtained the computed ν_1 and ν_3 frequencies which were, nonetheless, still too low by 19 cm^{-1} and too high by 17 cm^{-1}, respectively.

The observed [99,100,103] and computed [93,123, 127,130] anharmonic fundamental frequencies of HCO are compared in Table 5. Our VCI results based on the CC-CBS, hybrid QFF/grid PES are within 6 cm^{-1} of the experimental values. Again, the QFF representation of essentially the same PES leads to a much greater error of 30 cm^{-1} in ν_1 (C–H stretch), underscoring the utility of the hybrid representation, particularly, in this strongly anharmonic mode. Our variational method (VCI) indicates a small mode-mode coupling (ca. 5% in the wave function) between the first overtone of ν_2 and fundamental ν_1, which is in agreement with Bowman, Bittman, and Harding. While the previously computed frequencies listed in Table 5 generally agree well with the experiment, our CC-CBS values are in the most accurate and uniform agreement with the observed.

Table 6 compares the vibrationally-averaged structures and rotational constants with experimental values [102,131–133] for four low-lying states. The two sets of experimental zero-point structures differ from each other by hundredths of 1 Å or a few degrees.

The computed and observed structures agree within this inherent ambiguity in the experimental structural parameters. The computed rotational constants B and C also agree well with the observed within a few percents, whereas the computed rotational constant A suffers from a greater error of ca 5%, which is likely due to the neglect of rovibrational coupling in our computation. In fact, there are large discrepancies between the values of A in the (010) state between our prediction and Ref. [130], the origin of which is unclear. The computed values of B and C in the (010) state are similar to those in the (000) state, which is supported by experiments.

Table 5. Fundamental vibrational transition energies (in cm^{-1}) of HCO. The frequencies obtained with each of the seven PESs underlying the hybrid PES are given in Table S-2 of the supplementary online material.

Method	(100)[a]	(010)[a]	(001)[a]
Experiment	2434.48[b]	1080.76[c]	1868.17[c]
CC-CBS/hybrid/VCI[d]	2432	1079	1874
CC-CBS/QFF/VCI[d]	2403	1081	1870
$CCSD(2)_T$/aDZ/harmonic[d]	2683	1100	1848
Werner *et al.* [123]	2446	1081	1844
Serrano-Andrés, Forsberg, and Malmqvist [127]	2443	1072	1851
van Mourik, Dunning, and Peterson [93]	2461	1079	1866
Marenich and Boggs [130]	2416	1076	1885

[a]The vibrational quanta of the C–H stretch, bend, and C–O stretch, respectively.
[b]Dane *et al.* [99].
[c]Johns, McKellar, and Riggin [103].
[d]This work. The CC-CBS results are based on the CCSD/(aDZ, aTZ, aQZ), $CCSD(2)_T$/(aDZ, aTZ) and $CCSD(2)_{TQ}$/aDZ energies.

3.3. *HNO ($\tilde{X}^1A'$)*

Nitrosyl hydride or nitroxyl (HNO) in its $\tilde{X}^1A'$ state is a bent molecule of considerable importance in combustion chemistry as an intermediate in the formation of the air pollutant NO [134]. It has also recently gained attention in biochemistry and pharmacology as possible endogenous signaling species [135,136]. The observation of HNO was made initially in a flash photolysis [137] and subsequently by infrared spectroscopy in an Argon matrix [138]. It has been also observed in interstellar medium by radio detection [139]. Its fundamental vibrational frequencies were analyzed by electronic emission spectroscopy [140], absorption spectroscopy [141] and by electronic and vibrational emission spectroscopy [142]. They were confirmed by matrix-isolation infrared spectroscopy [143] and then improved in accuracy by laser Stark spectroscopy [144] which allowed a complete analysis of bending and C–O stretching fundamentals. Accurate measurements of the C–H stretch frequency were made by infrared absorption [145] and emission spectroscopy [146]. A number of other experimental studies on its microwave absorption [147,148] were reported on this molecule.

Among numerous computational studies on the PES of HNO [149–158], the anharmonic vibrational analysis by Dateo, Lee, and Schwenke [156] is the most pertinent to our work. They established a QFF in an internal coordinate using the CCSD(T)/cc-pVQZ method. The frequencies with the QFF were in good agreement with the observed, although the frequency of ν_1 (N–H stretch) was somewhat too low (by 17 cm^{-1}). Mordaunt *et al.* [158] employed MRCI with a triple-ζ basis set to scan the three lowest-lying PESs, which were subsequently scaled empirically to yield accurate fundamental frequencies. Also, HNO has the longest known N–H (equilibrium) bond length of 1.053 Å and

Table 6. Vibrationally-averaged bond lengths (in Å) and angle (in degrees) and rotational constants (A, B, and C) (in cm^{-1}) of HCO computed by the CC-CBS/hybrid/VCI method (experimental values, when available, in parentheses).

State[a]	(000)[a]	(100)[a]	(010)[a]	(001)[a]
r_{C-H}	1.141 (1.151[b], 1.125[c])	1.199	1.133	1.140
r_{C-O}	1.180 (1.178[b], 1.175[c])	1.176	1.180	1.188
a_{HCO}	124.3 (123.0[b], 125.0[c])	123.7	124.5	124.1
A	23.2 (24.3[d], 24.3[e])	20.9	23.6	23.1
B	1.48 (1.47[d], 1.49[e])	1.48	1.48 (1.50[c])	1.47
C	1.39 (1.37[d], 1.40[e])	1.38	1.40 (1.39[c])	1.38

[a]See footnote a of Table 5.
[b]Ogilvie [133].
[c]Brown and Ramsay [102].
[d]Hirota [132].
[e]Brown, Radford, and Sears [131].

its accurate structure has been under considerable scrutiny by Lee [159] and later by Demaison *et al.* [160,161].

Tables 7 and 8 list the anharmonic vibrational frequencies and vibrationally-averaged structures and rotational constants of HNO and compare them with the observed. Our CC-CBS PES in the hybrid QFF/grid representation reproduces the frequencies within $7\,cm^{-1}$ of the experimental values [144,145]. State-specific rotational constants were reported [133,137, 144,145] for all four states considered in Table 8. While the computed absolute values of the rotational constants can have errors in excess of a few percents, their variation across states (i.e. vibration-rotation coupling) is semi-quantitatively reproduced by theory. For instance, the (010) state has slightly greater values of A and B than the (001) state and this trend is predicted correctly by our calculation. Note that the order of these two states can be reversed in the harmonic approximation [159], causing an incorrect band assignment in the past. Our ability to compute state-specific rotational constants with sufficient accuracy will be helpful to avoid such problems. The vibrationally-averaged structural parameters are expected to be an order of magnitude more accurate than the rotational constants and should be within several thousandths of 1 Å of the true values. Our calculation favors the experimental zero-point geometry of Dalby [137].

Table 7. Fundamental vibrational transition energies (in cm^{-1}) of HNO. The frequencies obtained with each of the seven PESs underlying the hybrid PES are given in Table S-3 of the supplementary online material.

Method	(100)[a]	(010)[a]	(001)[a]
Experiment	2683.95[b]	1500.82[c]	1565.35[c]
CC-CBS/hybrid/VCI[d]	2683	1503	1572
CC-CBS/QFF/VCI[d]	2679	1499	1568
$CCSD(2)_T$/aDZ/harmonic[d]	2909	1531	1590
Dateo, Lee, and Schwenke [156]	2667	1507	1571
Mordaunt *et al.* [158]	2682[e]	1502[e]	1563[e]

[a]The vibrational quanta of the N–H stretch, bend, and N–O stretch, respectively.
[b]Johns, McKellar, and Weinberger [145].
[c]Johns and McKellar [144].
[d]This work. The CC-CBS results are based on the CCSD/(aDZ, aTZ, aQZ), $CCSD(2)_T$/(aDZ, aTZ) and $CCSD(2)_{TQ}$/aDZ energies.
[e]The PES was scaled empirically.

3.4. *HOO ($\tilde{X}^2A''$)*

The hydroperoxy radical (HOO) is an intermediate in the reaction $H + O_2 \rightarrow OH + O$, which has been referred to as 'the single most important chemical reaction in combustion' in [162]. It also plays a key role in atmospheric chemistry because the reverse reaction of the above is responsible for ozone destruction [163]. The reaction involves a conical intersection on the PES of HOO and its characterization is a challenging theoretical problem. Hence, there is an extensive literature on the PES of HOO; for a recent survey, the reader is referred to Xie *et al.* [164]. Several spectroscopic studies were performed to accurately measure the frequencies of the O–H stretch [165], bend [166,167], and C–O stretch [166,168–170]. Electron paramagnetic resonance measurements [171,172] also yielded ground state parameters.

Walch and Duchovic [173] employed MRCI to generate a PES expressed as a QFF and obtained the anharmonic frequencies of fundamentals, which

Table 8. Vibrationally-averaged bond lengths (in Å) and angle (in degrees) and rotational constants (A, B, and C) (in cm^{-1}) of HNO computed by the CC-CBS/hybrid/VCI method (experimental values, when available, in parentheses).

State[a]	(000)[a]	(100)[a]	(010)[a]	(001)[a]
r_{N-H}	1.075 (1.09[b], 1.063[c])	1.124	1.071	1.075
r_{N-O}	1.213 (1.209[b], 1.212[c])	1.208	1.217	1.221
a_{HNO}	108.4 (108.0[b], 108.6[c])	108.7	108.4	108.5
A	18.2 (18.5[d,e])	16.8 (17.7[d])	18.3 (18.8[d,e])	18.2 (18.6[d,e])
B	1.40 (1.41[d,e])	1.41 (1.42[d])	1.39 (1.41[d,e])	1.38 (1.40[d,e])
C	1.30 (1.31[d,e])	1.30 (1.31[d])	1.30 (1.29[d], 1.30[e])	1.29 (1.30[d], 1.29[e])

[a]See footnote a of Table 7.
[b]Ogilvie [133].
[c]Dalby [137].
[d]Johns, McKellar, and Weinberger [145].
[e]Johns and McKellar [144].

deviated from the observed by up to 108 cm^{-1}. Xu *et al*. [174] computed energies at 15000 geometries by MRCI with the Davidson correction with the aug-cc-pVQZ basis set. They solved the vibrational Schrödinger equation by the Lanczos method [175] and obtained vibrational energies up to 7000 cm^{-1}. They subsequently improved their PES and achieved the vibrational state calculations up to the dissociation limit [164,176,177]. Their computed frequencies of the fundamentals [176] were in excellent agreement with the observed (within 8 cm^{-1}). Among the other computational studies, those that are closely related to this one are [178–188].

Table 9. Fundamental vibrational transition energies (in cm^{-1}) of HOO. The frequencies obtained with each of the seven PESs underlying the hybrid PES are given in Table S-4 of the supplementary online material.

Method	(100)[a]	(010)[a]	(001)[a]
Experiment	3436.20[b]	1391.75[c]	1097.63[d]
CC-CBS/hybrid/VCI[e]	3447	1399	1121
CC-CBS/QFF/VCI[e]	3424	1400	1118
$CCSD(2)_T$/aDZ/harmonic[e]	3628	1428	1080
Walch and Duchovic [173]	3356	1415	1206
Xu *et al*. [176]	3433	1389	1090

[a]The vibrational quanta of the O–H stretch, bend, and O–O stretch, respectively.
[b]Yamada, Endo, and Hirota [165].
[c]Nagai, Endo, and Hirota [167].
[d]Johns, McKellar, and Riggin [169].
[e]This work. The CC-CBS results are based on the CCSD/(aDZ, aTZ, aQZ), $CCSD(2)_T$/(aDZ, aTZ) and $CCSD(2)_{TQ}$/aDZ energies.

Our calculated anharmonic frequencies agree with experiment [165,167,169] within 23 cm^{-1}. The errors are small but somewhat larger (especially for ν_3 or the O–O stretch) than those in the other molecules studied in this work. Since the full VCI method is used for this radical and the differences between QFF and hybrid QFF/grid representations are no greater than the other cases, the electronic structure methods are likely the primary source of the errors. Although the CC-CBS limits are supposed to be reached, the extrapolation formulae assume the validity of perturbation treatments of triple and quadruple excitations. It is possible that this assumption is not entirely valid for this radical at certain geometries. Comparing our vibrational state energies with the results of Xu *et al*. [176], we find that both studies are in perfect agreement in the assignments of the states up to 5500 cm^{-1}. Below this threshold, the experimental energies tend to fall in between our computed values and those of Xu *et al*., the latter being always the lower bound. This suggests that our PES is slightly more strongly curved than the true PES.

Notwithstanding the slight increase in the errors in the anharmonic frequencies, our calculations reproduce the variation in the rotational constants with respect to vibrational states well. The variations of B and C are smaller but their trends are accurately predicted. The computed r_{O-O} and a_{HOO} are in agreement with the observed, whereas it is hard to gauge the accuracy of r_{O-H} because the experimental values are scattered. We expect that our computed structures have uniform accuracy of a few tenths of 1% regardless of the types of atoms involved or vibrational states.

Table 10. Vibrationally-averaged bond lengths (in Å) and angle (in degrees) and rotational constants (A, B, and C) (in cm^{-1}) of HOO computed by the CC-CBS/hybrid/VCI method (experimental values, when available, in parentheses).

State[a]	(000)[a]	(100)[a]	(010)[a]	(001)[a]
r_{O-H}	0.984 (1.006[b], 0.977[c])	1.022	0.977	0.983
r_{O-O}	1.333 (1.333[b], 1.334[c])	1.330	1.337	1.345
a_{HOO}	104.6 (104.4[b], 104.1[c])	105.0	104.9	104.0
A	20.2 (20.4[d])	18.8 (19.6[e])	20.5 (21.0[f])	20.1 (20.3[g])
B	1.12 (1.12[d])	1.12 (1.12[e])	1.11 (1.12[f])	1.10 (1.11[g])
C	1.06 (1.06[d])	1.06 (1.06[e])	1.05 (1.05[f])	1.04 (1.04[g])

[a]See footnote a of Table 9.
[b]Ogilvie [133].
[c]Barnes, Brown, and Radford [172].
[d]Barnes *et al*. [171].
[e]Yamada, Endo, and Hirota [165].
[f]Nagai, Endo, and Hirota [167].
[g]Johns, McKellar, and Riggin [169].

3.5. HOO^- ($\tilde{X}^1A'$)

In contrast to its neutral counterpart, the literature on the hydroperoxy anion (HOO^-) is scarce. There in only one report on its photoelectron spectra [189], which provides an approximate frequency of $775 \pm 250\,cm^{-1}$ for ν_3 (O–O stretch). On the theory side, Horn *et al*. [190] obtained a 144-point PES with the CCSD(T)/aug-cc-pVTZ method and predicted the anharmonic frequencies of the fundamentals listed in Table 11. Chan and Hamilton. [191] performed QCISD(T)/6-311++G(2df,pd) energy calculations at 1535 geometries and fitted the PES with a 120-parameter analytic function with a root mean square error of $223\,cm^{-1}$. The predicted frequencies of the fundamentals obtained with this PES differ from those of Horn *et al*. by up to $80\,cm^{-1}$. Botschwina and Horn [185] upgraded the previous results [190] by increasing the electronic structure theory level to CCSD(T)/aug-cc-pVQZ. The predicted frequencies were close (within $11\,cm^{-1}$) to the values of Horn *et al*. Computational simulations of their photoelectron spectra were also performed for this anion [192–194].

Our predicted values of the fundamental frequencies display the same general trend observed for the other bent triatomic molecules: small anharmonicity in ν_2 and ν_3 frequencies and a slightly greater improvement in the ν_1 frequency by the hybrid QFF/grid representation. Our best theoretical predictions (CC-CBS/hybrid/VCI) agree with those of Botschwina and Horn [185] within $11\,cm^{-1}$ and with those of Horn *et al*. [190] within $15\,cm^{-1}$. They differ from the values suggested by Chan and Hamilton [191] by 78 and $54\,cm^{-1}$ in ν_1 and ν_3, respectively. As in the case with the neutral, the ν_3 (O–O stretch) frequency shows slightly slower convergence with respect to the electronic structure level and the basis set size (see Table S-5). We, therefore, expect that our predicted frequencies are approximately within 10, 10, and $20\,cm^{-1}$ of the true ν_1, ν_2, and ν_3 frequencies, respectively. The uncertainty in the observed ν_3 frequency [189] appears to be much smaller than $250\,cm^{-1}$.

Our predicted zero-point bond lengths (Table 12) agree well with the observed values [189], whereas the computed bond angle is considerably smaller than the observed. The disagreement is due the fact that the bond angle (and one of the bond lengths) was simply assumed rather than determined experimentally [189]. The values reported by other theoretical studies also favour our prediction [185,190–194]. Unlike the experimental determination of these parameters via the interpretation of the spectra, our computed values are expected to have uniform accuracy across different parameters. The predicted rotational constants will be helpful for band assignments, when state-specific rotational constants of HOO^- are observed.

Table 11. Fundamental vibrational transition energies (in cm^{-1}) of HOO^-. The frequencies obtained with each of the seven PESs underlying the hybrid PES are given in Table S-5 of the supplementary online material.

Method	(100)[a]	(010)[a]	(001)[a]
Experiment	...	...	775 ± 250[b]
CC-CBS/hybrid/VCI[c]	3587	1088	739
CC-CBS/QFF/VCI[c]	3561	1084	742
$CCSD(2)_T$/aDZ/harmonic[c]	3768	1109	725
Horn *et al*. [190]	3585	1073	728
Chan and Hamilton [191]	3665	1079	685
Botschwina and Horn [185]	3581	1084	728

[a]The vibrational quanta of the O–H stretch, bend, and O–O stretch, respectively.
[b]Oakes, Harding, and Ellison [189].
[c]This work. The CC-CBS results are based on the CCSD/(aDZ, aTZ, aQZ), $CCSD(2)_T$/(aDZ, aTZ) and $CCSD(2)_{TQ}$/aDZ energies.

3.6. CH_3^+ ($\tilde{X}^1A_1'$)

The methyl cation is among the most important carbonium ions. It is highly reactive and commonly found in the discharges from hydrocarbon combustion. CH_3^+ in its $\tilde{X}^1A_1'$ state has a planar equilibrium geometry belonging to the D_{3h} group. Despite its importance, there is a lack of high resolution spectroscopic data for CH_3^+ primarily because of its polymerization in discharges [195]. Oka and co-workers [195–197] observed the accurate frequency of the degenerate C–H stretch (ν_3) by infrared spectroscopy. There have also been reports [198–201] on the frequencies of the umbrella (out-of-plane or OPLA)

Table 12. Vibrationally-averaged bond lengths (in Å) and angle (in degrees) and rotational constants (A, B, and C) (in cm^{-1}) of HOO^- computed by the CC-CBS/hybrid/VCI method (experimental values, when available, in parentheses).

State[a]	(000)[a]	(100)[a]	(010)[a]	(001)[a]
r_{O-H}	0.969 (0.97[b,c])	1.006	0.958	0.967
r_{O-O}	1.525 (1.50[b])	1.520	1.535	1.541
a_{HOO}	97.7 (104[b,c])	98.5	97.2	96.7
A	19.5	18.2	19.9	19.5
B	0.87	0.87	0.86	0.85
C	0.83	0.83	0.82	0.82

[a]See footnote a of Table 11.
[b]Oakes, Harding, and Ellison [189].
[c]Assumed values [189].

mode (ν_2) and deformation mode (ν_4) primarily with photoelectron spectroscopy. However, no observed frequency of the non-degenerate C–H stretch (ν_1) has been available yet.

Following earlier computational studies [202–207], Yu and Sears [208] performed a CC-CBS extrapolation akin to ours in the PES scan of CH_3^+. They employed the approach of Halkier *et al.* [209] based on the CCSD(T)/cc-pVTZ and cc-pVQZ energies at 227 geometries. The PES was expressed as a QFF in an internal coordinate. The raw PES was found to overestimate the frequencies of some of the fundamentals by $30\,cm^{-1}$ and a coordinate scaling was applied to achieve the best overall agreement. The frequencies of Yu and Sears in Table 13 correspond to the scaled PES and experimental frequencies are taken from [195,201].

Anti-symmetric C–H stretch (ν_3) and deformation (ν_4) modes of CH_3^+ are doubly degenerate due to the D_{3h} symmetry. The 3MR approximation and our use of C_{2v} computational symmetry throughout the calculations can cause these degenerate modes to be treated in a non-equivalent manner. However, the lifting of degeneracy still stays about $1\,cm^{-1}$ for both modes with the grid and hybrid QFF/grid PES representations. On the other hand, in the QFF calculations, the degeneracy of the ν_3 mode is lifted by $10\,cm^{-1}$, while that of the deformation mode is hardly affected. This is probably due to inevitable errors in finite-difference numerical differentiation used to obtain the QFF that are particularly large for ν_3 which experiences a strongly anharmonic Morse-type potential. We simply report the average of the two frequencies for the QFF results. It should be noted that the hybrid QFF/grid method resists to such numerical errors and preserves the degeneracy about $1\,cm^{-1}$, which is another advantage of our proposed scheme.

Although our CC-CBS calculations do not involve any coordinate scaling, their frequencies are in generally good agreement with the predictions of Yu and Sears. Hence, $2940 \pm 20\,cm^{-1}$ serves as a reliable predicted value of the frequency of ν_1, the experimental value of which is still unknown. The frequencies of the two other modes (ν_2 and ν_4) are exceedingly close to each other and the correct assignment on the basis of the observed and calculated frequencies alone is difficult. Here, our vibrationally-averaged rotational constants (shown in Table 14) can be useful in assisting in experimental spectroscopic studies. The theory predicts the C–H bond length and hence the values of both B and C are noticeably different between (0100) and (0001) states, which can, therefore, be spectroscopically discernible by rotational constants. The vibrational state dependence of the measured values of B and C are consistent with our prediction, although the absolute computed values of B can be erroneous by 2%.

Table 13. Fundamental vibrational transition energies (in cm^{-1}) of CH_3^+. The frequencies obtained with each of the seven PESs underlying the hybrid PES are given in Table S-6 of the supplementary online material.

Method	(1000)[a]	(0100)[a]	(0010)[a]	(0001)[a]
Experiment	···	1359 ± 7[b]	3108.38[c]	1370 ± 7[b]
CC-CBS/ hybrid/VCI[d]	2940	1383	3096	1384
CC-CBS/ QFF/VCI[d]	2933	1383	3099[e]	1385
$CCSD(2)_T$/ aDZ/harmonic[d]	3037	1418	3247	1429
Yu and Sears [208]	2942[f]	1378[f]	3108[f]	1387[f]

[a]The vibrational quanta of the symmetric C–H stretch (a_1'), umbrella (a_2''), anti-symmetric C–H stretch (e'), and deformation (e'), respectively.
[b]Liu, Gross, and Suits [201].
[c]Crofton *et al.* [195].
[d]This work. The CC-CBS results are based on the CCSD/(aDZ, aTZ, aQZ), $CCSD(2)_T$/(aDZ, aTZ) and $CCSD(2)_{TQ}$/aDZ energies.
[e]The average of 3094 and $3105\,cm^{-1}$ (see text).
[f]The PES was scaled empirically.

Table 14. Vibrationally-averaged C–H bond length (in Å) and rotational constants (B and C) (in cm^{-1}) of CH_3^+ computed by the CC-CBS/hybrid/VCI method (experimental values, when available, in parentheses).

State[a]	(0000)[a]	(1000)[a]	(0100)[a]	(0010)[a]	(0001)[a]
r_{C-H}	1.102 (1.1[b])	1.112	1.100	1.113[c]	1.101[d]
B	9.18 (9.36[e])	9.02	9.21 (9.1[f])	9.00[g]	9.20[h] (9.1[f])
C	4.59 (4.61[b])	4.51	4.61	4.50	4.60

[a]See footnote a of Table 13.
[b]Crofton *et al.* [195].
[c]One of the degenerate states has the bond lengths of 1.1245, 1.1079 and 1.1079 Å and bond angles of 119.83, 119.83, and 120.33 degrees. The other has the bond lengths of 1.1020, 1.1187 and 1.1187 Å and bond angles of 120.17, 120.17, and 119.65 degrees.
[d]One of the degenerate states has the bond lengths of 1.1030, 1.0997 and 1.0997 Å and bond angles of 119.67, 119.67, and 120.67 degrees. The other has the bond lengths of 1.0983, 1.1020 and 1.1020 Å and bond angles of 120.33, 120.33, and 119.35 degrees.
[e]Jagod *et al.* [197].
[f]Liu, Gross, and Suits [201].
[g]The average of 9.06 and $8.94\,cm^{-1}$.
[h]The average of 9.24 and $9.16\,cm^{-1}$.

The wave functions of the (0010) and (0001) states transform as e' and are doubly degenerate. The vibrationally-averaged structures in these states belong to of the C_{2v} group, which is the Abelian subgroup of the D_{3h} and the computational symmetry used in our calculation. For instance, one of the degenerate (0010) states has the C–H bond lengths of 1.1020, 1.1187, and 1.1187 Å and the HCH bond angles of 120.17, 120.17, and 119.65 degrees, whereas the other has the bond lengths of 1.1245, 1.1079, and 1.1079 Å and the bond angles of 119.83, 119.83, and 120.33 degrees. Because the degenerate states can be rotated by an arbitrary unitary transformation, these structures by themselves do not have particular physical significance. However, the averages of the C–H bond lengths (1.113 Å) and bond angles (120.0 degree) are invariant to this rotation and it is meaningful to compare these averages with the structures of other states. In the (0010) state, the average C–H bond length experiences a net increase of 0.01 Å from the zero-point value, reflecting the Morse-like shape of the C–H stretch. In our rigid-rotor treatment, the rotational constants of a degenerate state can be computed either from the averaged and hence D_{3h} structure or from two C_{2v} structures and then averaged afterwards. The values in Table 14 were obtained in the latter procedure. Owing to this ambiguity in our rigid-rotor treatment, the computed rotational constants are expected to be less accurate than the vibrationally-averaged structures.

3.7. CH_3 ($\tilde{X}^2A_2''$)

As its cationic counterpart, the methyl radical (CH_3) in the $\tilde{X}^2A_2''$ state has a planar structure that belongs to the D_{3h} group. The planarity was a subject of controversy partly because of the rather small frequency (606 cm^{-1}) of the umbrella (OPLA) vibration (ν_2) that had been viewed as an indication of non-planar geometry until the planarity was confirmed spectroscopically by Yamada, Hirota, and Kawaguchi [210]. The frequency of the symmetric C–H stretch fundamental (ν_1) was the subject of many spectroscopic studies [211–215]. Those of the umbrella (OPLA) (ν_2) [210,216,217] and anti-symmetric C–H stretch (ν_3) [218–223] were also measured accurately. For the deformation (ν_4), approximate values of its frequency were obtained [224–227] by the matrix isolation technique and they were in the range of 1396 to 1403 cm^{-1}. No gas-phase measurements have so far been reported for this mode.

A considerable number of computational studies on CH_3 were reported [202–204,228–236], but most of them focused on its electronic structure, geometry, and frequencies in the harmonic approximation and only a few were concerned with anharmonic vibrations. Surratt and Goddard [203] solved the one-dimensional vibrational Schrödinger problem along the umbrella mode (ν_2), assuming the planar equilibrium geometry and obtained the frequency of 585 cm^{-1}, which was in good agreement with the observed (606 cm^{-1}). Botschwina, Flesch, and Meyer [231] obtained a QFF in just two vibrational degrees of freedom with the coupled electron pair approximation (CEPA) method. Their computed frequencies of ν_1 and ν_2 were 63 and 8 cm^{-1} too high and too low, respectively. More recently, Roberto-Neto, Chakravorty, and Machado [236] performed the CBS extrapolation of the calculated C–H bond length and harmonic frequencies calculated at the CCSD(T) level. According to their study, large anharmonic contributions of 80–150 cm^{-1} exist in ν_1, ν_2, and ν_3.

Table 15 compares our computed frequencies with the observed [210,213,218,224,226] as well as the previous calculations [203,231,236]. Our CC-CBS/hybrid/VCI frequencies are in good agreement with the observed although the error in the frequency of ν_2 (42 cm^{-1}) appears to be slightly outside the usual range. This may be due to a vibronic coupling between the ground and excited electronic states, as suggested by Burdett [237] and Yamada *et al.* [210]. Another possible source of the error is the neglect of the rovibrational coupling in this study, which is known to be generally greater in out-of-plane modes [56]. Our predicted frequency of ν_4 is somewhat smaller than those measured in the matrices. A part of the error might be ascribed to matrix shifts, which are positive and do not exceed ca 20 cm^{-1} for ν_4.

Table 16 compares the vibrationally-averaged bond lengths and rotational constants with the observed [210,213,218,223]. The latter is available for three of the low-lying vibrationally excited states as well as for the zero-point vibrational state. The computed values of C (corresponding to the rotations around the C_3 axis) reproduce the observed trend across different states reasonably well, although the agreement cannot be said to be quantitative. The theory also correctly predicts the increase in the C–H bond lengths in the (1000) state, which is clearly due to the Morse-like shape of the C–H stretch potential. However, it completely fails in reproducing even the signs of variation in the C–H bond lengths upon excitation to the (0100) and (0010) states. Although the bending vibrations usually decrease the average bond lengths and our result for the (0100) state appears to follow this trend, the experimental result [213] indicates the opposite. The predicted values of B do not agree well

Table 15. Fundamental vibrational transition energies (in cm^{-1}) of CH_3. The frequencies obtained with each of the seven PESs underlying the hybrid PES are given in Table S-7 of the supplementary online material.

Method	(1000)[a]	(0100)[a]	(0010)[a]	(0001)[a]
Experiment	3004.4[b]	606.45[c]	3160.82[d]	(1396[e], 1403[f])
CC-CBS/hybrid/VCI[g]	3002	565	3139	1377
CC-CBS/QFF/VCI[g]	2998	580	3139[h]	1375
$CCSD(2)_T$/aDZ/harmonic[g]	3103	498	3292	1407
Surratt and Goddard [203]	...	585	...	...
Botschwina, Flesch, and Meyer [231]	3067	598	...	...
Roberto-Neto, Chakravorty, and Machado [236]	3129[i]	524[i]	3313[i]	1424[i]

[a]The vibrational quanta of the symmetric C–H stretch (a_1'), umbrella (a_2''), anti-symmetric C–H stretch (e'), and deformation (e'), respectively.
[b]Triggs *et al*. [213].
[c]Yamada, Hirota, and Kawaguchi [210].
[d]Amano *et al*. [218].
[e]A matrix-isolation study by Snelson [224].
[f]A matrix-isolation study by Momose *et al*. [226].
[g]This work. The CC-CBS results are based on the CCSD/(aDZ, aTZ, aQZ), $CCSD(2)_T$/(aDZ, aTZ) and $CCSD(2)_{TQ}$/aDZ energies.
[h]The average of 3133 and 3144 cm^{-1} (see text).
[i]CCSD(T)/CBS in the harmonic approximation.

Table 16. Vibrationally-averaged C–H bond length (in Å) and rotational constants (B and C) (in cm^{-1}) of CH_3 computed by the CC-CBS/hybrid/VCI method (experimental values, when available, in parentheses).

State[a]	(0000)[a]	(1000)[a]	(0100)[a]	(0010)[a]	(0001)[a]
r_{C-H}	1.087 (1.079[b])	1.097 (1.084[b])	1.080 (1.097[b])	1.098[c] (1.085[b])	1.086[d]
B	9.43 (9.58[e])	9.26 (9.49[b])	9.56 (9.26[e])	9.26[f] (9.47[e,g,h])	9.47[i]
C	4.72 (4.74[e])	4.63 (4.69[b])	4.78 (4.81[e])	4.63 (4.70[g,h])	4.73

[a]See footnote a of Table 15.
[b]Triggs *et al*. [213].
[c]One of the degenerate states has the bond lengths of 1.0864, 1.1031 and 1.1031 Å and bond angles of 120.27, 120.27, and 119.47 degrees. The other has the bond lengths of 1.1086, 1.0925, and 1.0925 Å and bond angles of 119.75, 119.75, and 120.49 degrees.
[d]One of the degenerate states has the bond lengths of 1.0882, 1.0843 and 1.0843 Å and bond angles of 119.68, 119.68, and 120.65 degrees. The other has the bond lengths of 1.0826, 1.0870, and 1.0870 Å and bond angles of 120.32, 120.32, and 119.36 degrees.
[e]Yamada, Hirota, and Kawaguchi [210].
[f]The average of 9.30 and 9.21 cm^{-1}.
[g]Amano *et al*. [218].
[h]The average of 9.50 and 9.43 cm^{-1}.
[i]Kawaguchi [223].

with the observed for almost all states considered. This may underscore the significance of the rovibrational couplings and also possibly be related to the aforementioned vibronic coupling operating in this molecule.

4. Concluding remarks

An accurate and predictive scheme to compute low-lying vibrational wave functions and energies of polyatomic molecules is proposed with applications to the seven key species of hydrocarbon combustion. The results have been compared with experimental values, whenever the latter are available. The agreement between theory and experiment for fundamental frequencies is within 11 cm^{-1} (the mean absolute deviation) for all the molecules. When only the triatomic molecules are considered, this deviation reduces to 7 cm^{-1}; the agreement in CH_3^+ and CH_3 is slightly worse partly because of the 3MR approximation and larger rovibrational couplings. For HOO^-, CH_3^+, and CH_3, of which some or all of experimental data for the fundamental transition frequencies are unknown, our predicted frequencies are expected to be no more than 20 cm^{-1} away from the

correct values. In most cases, the vibrationally-averaged structural parameters and rotational constants reproduce their trend observed across different vibrational states. However, there have been cases where the vibrationally-averaged rotational constants obtained in the rigid-rotor approximation are qualitatively incorrect.

The core of this scheme is the converged PESs in wide areas of the geometry space obtained by combining different electronic structure methods [CCSD, CCSD(2)$_T$, and CCSD(2)$_{TQ}$] and basis sets (aDZ, aTZ, and aQZ) to extrapolate the CC-CBS limits. The reader is referred to Tables S1–S7 of the supplementary online material for the results of some of these individual calculations. This CC-CBS extrapolation is feasible because a common set of normal coordinates is used. The PESs generated by this method are represented by QFFs and numerical values on rectilinear grids, but the new hybrid representation has also been proposed to avoid the shortcomings of the former. This hybrid representation has been shown to be a uniform and inexpensive improvement over QFFs or grid PESs. The vibrational Schrödinger equation has been solved by VCI, which is exact for the triatomic molecules (all configurations are included) and sufficiently converged for the tetratomic molecules.

The approximations involved in this scheme are the Born–Oppenheimer approximation, the neglect of rovibrational coupling (centrifugal distortion and Coriolis coupling), non-relativistic treatment, the neglect of core-correlation effects, the higher-order electron-correlation and mode-mode coupling, etc. This scheme is inadequate for highly-excited vibrations or very large-amplitude vibrations owing to our dependence on normal coordinates. Although the use of internal coordinates and keeping all the terms in Watson Hamiltonian can avoid such problems in triatomic molecules, our scheme is expected to be more widely and generally applicable to larger polyatomic molecules with small amplitude vibrations.

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References

[1] H.F. Schaefer III, Science **231**, 1100 (1986).
[2] S. Hirata and K. Yagi, Chem. Phys. Lett. **464**, 123 (2008).
[3] T.H. Dunning Jr, J. Chem. Phys. **90**, 1007 (1989).
[4] R.A. Kendall, T.H. Dunning Jr, and R.J. Harrison, J. Chem. Phys. **96**, 6796 (1992).
[5] V. Rodriguez-Garcia, K. Yagi, K. Hirao, S. Iwata, and S. Hirata, J. Chem. Phys. **125**, 014109 (2006).
[6] V. Rodriguez-Garcia, S. Hirata, K. Yagi, K. Hirao, T. Taketsugu, I. Schweigert, and M. Tasumi, J. Chem. Phys. **126**, 124303 (2007).
[7] S. Hirata, K. Yagi, S.A. Perera, S. Yamazaki, and K. Hirao, J. Chem. Phys. **128**, 214305 (2008).
[8] G.D. Purvis III and R.J. Bartlett, J. Chem. Phys. **76**, 1910 (1982).
[9] G.E. Scuseria, T.J. Lee, and H.F. Schaefer III, Chem. Phys. Lett. **130**, 236 (1986).
[10] S. Hirata, P.-D. Fan, A.A. Auer, M. Nooijen, and P. Piecuch, J. Chem. Phys. **121**, 12197 (2004).
[11] T.H. Dunning Jr, J. Phys. Chem. A **104**, 9062 (2000).
[12] J. Rychlewski, *Explicitly Correlated Wave Functions in Chemistry and Physics* (Kluwer Academic Publishers, Dordrecht, 2003).
[13] T. Shiozaki, M. Kamiya, S. Hirata, and E.F. Valeev, Phys. Chem. Chem. Phys. **10**, 3358 (2008).
[14] T. Shiozaki, M. Kamiya, S. Hirata, and E.F. Valeev, J. Chem. Phys. **129**, 071101 (2008).
[15] T. Shiozaki, M. Kamiya, S. Hirata, and E.F. Valeev, J. Chem. Phys. **130**, 054101 (2009).
[16] J.O. Jung and R.B. Gerber, J. Chem. Phys. **105**, 10332 (1996).
[17] S. Carter, S.J. Culik, and J.M. Bowman, J. Chem. Phys. **107**, 10458 (1997).
[18] K. Yagi, T. Taketsugu, K. Hirao, and M.S. Gordon, J. Chem. Phys. **113**, 1005 (2000).
[19] K. Yagi, T. Taketsugu, and K. Hirao, J. Chem. Phys. **116**, 3963 (2002).
[20] K. Yagi, K. Hirao, T. Taketsugu, M.W. Schmidt, and M.S. Gordon, J. Chem. Phys. **121**, 1383 (2004).
[21] M.S. Schuurman, W.D. Allen, P.V.R. Schleyer, and H.F. Schaefer III, J. Chem. Phys. **122**, 104302 (2005).
[22] M.S. Schuurman, W.D. Allen, and H.F. Schaefer III, J. Comput. Chem. **26**, 1106 (2005).
[23] A.C. Simmonett, F.A. Evangelista, W.D. Allen, and H.F. Schaefer III, J. Chem. Phys. **127**, 014306 (2007).
[24] X. Huang and T.J. Lee, J. Chem. Phys. **129**, 044312 (2008).
[25] A.C. Simmonett, H.F. Schaefer III, and W.D. Allen, J. Chem. Phys. **130**, 044301 (2009).
[26] R. Burcl, S. Carter, and N.C. Handy, Chem. Phys. Lett. **373**, 357 (2003).
[27] O. Christiansen, Phys. Chem. Chem. Phys. **9**, 2942 (2007).
[28] W. Meyer, P. Botschwina, and P. Burton, J. Chem. Phys. **84**, 891 (1986).

[29] G.M. Chaban, J.O. Jung, and R.B. Gerber, J. Chem. Phys. **111**, 1823 (1999).
[30] S. Irle and J.M. Bowman, J. Chem. Phys. **113**, 8401 (2000).
[31] E.B. Wilson Jr, J.C. Decius, and P.C. Cross, *Molecular Vibrations* (McGraw-Hill, New York, 1955).
[32] I.M. Mills and A.G. Robiette, Mol. Phys. **56**, 743 (1985).
[33] G.D. Carney, L.L. Sprandel, and C.W. Kern, Adv. Chem. Phys. **37**, 305 (1978).
[34] J.M. Bowman, J. Chem. Phys. **68**, 608 (1978).
[35] J.M. Bowman, Acc, Chem. Res. **19**, 202 (1986).
[36] M.A. Ratner and R.B. Gerber, J. Phys. Chem. **90**, 20 (1986).
[37] L.S. Norris, M.A. Ratner, A.E. Roitberg, and R.B. Gerber, J. Chem. Phys. **105**, 11261 (1996).
[38] K. Yagi, S. Hirata, and K. Hirao, J. Chem. Phys. **127**, 034111 (2007).
[39] J.M. Bowman, K. Christoffel, and F. Tobin, J. Phys. Chem. **83**, 905 (1979).
[40] K. Yagi, *SINDO, Version 2.0* (University of Tokyo, Tokyo, Japan, 2006).
[41] O. Christiansen, J. Chem. Phys. **120**, 2149 (2004).
[42] T.J. Lee and G.E. Scuseria, in *Quantum Mechanical Electronic Structure Calculations with Chemical Accuracy*, edited by S.R. Langhoff (Kluwer Academic, Dordrecht, 1995).
[43] A. Császár, W.D. Allen, Y. Yamaguchi, and H.F. Schaefer III, in *Computational Molecular Spectroscopy*, edited by P. Jensen and P.R. Bunker (John Wiley & Sons, Chichester, 2000).
[44] O.L. Polyansky, A.G. Császár, S.V. Shirin, N.F. Zobov, P. Barletta, J. Tennyson, D.W. Schwenke, and P.J. Knowles, Science **299**, 539 (2003).
[45] J.A. Pople, M. Head-Gordon, D.J. Fox, K. Raghavachari, and L.A. Curtiss, J. Chem. Phys. **90**, 5622 (1989).
[46] K.A. Peterson, D.E. Woon, and T.H. Dunning Jr, J. Chem. Phys. **100**, 7410 (1994).
[47] J.M.L. Martin and T.J. Lee, Chem. Phys. Lett. **258**, 136 (1996).
[48] T. Helgaker, W. Klopper, H. Koch, and J. Noga, J. Chem. Phys. **106**, 9639 (1997).
[49] S. Hirata, T. Yanai, W.A. de Jong, T. Nakajima, and K. Hirao, J. Chem. Phys. **120**, 3297 (2004).
[50] T.P. Straatsma, E. Aprà, T.L. Windus, E.J. Bylaska, W.A. de Jong, S. Hirata, M. Valiev, M.T. Hackler, L. Pollack, R.J. Harrison, M. Dupuis, D.M.A. Smith, J. Nieplocha, V. Tipparaju, M. Krishnan, A.A. Auer, E. Brown, G. Cisneros, G.I. Fann, H. Früchtl, J. Garza, K. Hirao, R. Kendall, J.A. Nichols, K. Tsemekhman, K. Wolinski, J. Anchell, D. Bernholdt, P. Borowski, T. Clark, D. Clerc, H. Dachsel, M. Deegan, K. Dyall, D. Elwood, E. Glendening, M. Gutowski, A. Hess, J. Jaffe, B. Johnson, J. Ju, R. Kobayashi, R. Kutteh, Z. Lin, R. Littlefield, X. Long, B. Meng, T. Nakajima, S. Niu, M. Rosing, G. Sandrone, M. Stave, H. Taylor, G. Thomas, J.v. Lenthe, A. Wong, and Z. Zhang, *NWChem, A Computational Chemistry Package for Parallel Computers, Version 4.7* (Pacific Northwest National Laboratory, Richland, WA, USA, 2005).
[51] J.F. Stanton, J. Gauss, J.D. Watts, M. Nooijen, N. Oliphant, S.A. Perera, P.G. Szalay, W.J. Lauderdale, S.A. Kucharski, S.R. Gwaltney, S. Beck, A. Balková, D.E. Bernhold, K.K. Baeck, P. Rozyczko, H. Sekino, C. Hober, and R.J. Bartlett, *ACES II, a program product of the Quantum Theory Project* (University of Florida, Gainesville, FL, USA, 1992).
[52] J.K.G. Watson, Mol. Phys. **15**, 479 (1968).
[53] J.K.G. Watson, Mol. Phys. **19**, 465 (1970).
[54] E. Mátyus, G. Czakó, B.T. Sutcliffe, and A.G. Császár, J. Chem. Phys. **127**, 084102 (2007).
[55] J.M. Bowman, S. Carter, and X. Huang, Int. Rev. Phys. Chem. **22**, 533 (2003).
[56] P. Carbonniere and V. Barone, Chem. Phys. Lett. **392**, 365 (2004).
[57] R.J. Whitehead and N.C. Handy, J. Mol. Spectrosc. **55**, 356 (1975).
[58] R.J. Whitehead and N.C. Handy, J. Mol. Spectrosc. **59**, 459 (1976).
[59] L.J. Allamandola, J. Mol. Struct. **157**, 255 (1987).
[60] J. Warnatz, in *Combustion Chemistry*, edited by W.C. Gardiner Jr (Springer-Verlag, Berlin, 1984).
[61] D. Buhl and L.E. Snyder, Nature **228**, 267 (1970).
[62] W. Klemperer, Nature **227**, 1230 (1970).
[63] U. Wahlgren, B. Liu, P.K. Pearson, and H.F. Schaefer III, Nature (London) Phys. Sci. **246**, 4 (1973).
[64] L.E. Snyder, J.M. Hollis, B.L. Ulich, F.J. Lovas, and D. Buhl, Bull. Am. Astron. Soc. **7**, 497 (1975).
[65] R.C. Woods, T.A. Dixon, R.J. Saykally, and P.G. Szanto, Phys. Rev. Lett. **35**, 1269 (1975).
[66] M. Bogey, C. Demuynck, and J.L. Destombes, Mol. Phys. **43**, 1043 (1981).
[67] K.V.L.N. Sastry, E. Herbst, and F.C. De Lucia, J. Chem. Phys. **75**, 4169 (1981).
[68] R.C. Woods, R.J. Saykally, T.G. Anderson, T.A. Dixon, and P.G. Szanto, J. Chem. Phys. **75**, 4256 (1981).
[69] E. Hirota and Y. Endo, J. Mol. Spectrosc. **127**, 527 (1988).
[70] R.C. Woods, Philos. Trans. R. Soc. London, A **324**, 141 (1988).
[71] V. Lattanzi, A. Walters, B.J. Drouin, and J.C. Pearson, Astrophys. J. **662**, 771 (2007).
[72] F. Tinti, L. Bizzocchi, C. Degli Esposti, and L. Dore, Astrophys. J. Lett. **669**, L113 (2007).
[73] T. Hirao, S. Yu, and T. Amano, J. Mol. Spectrosc. **248**, 26 (2008).
[74] C.S. Gudeman, M.H. Begemann, J. Pfaff, and R.J. Saykally, Phys. Rev. Lett. **50**, 727 (1983).
[75] T. Amano, J. Chem. Phys. **79**, 3595 (1983).
[76] P.B. Davies, P.A. Hamilton, and W.J. Rothwell, J. Chem. Phys. **81**, 1598 (1984).
[77] P.B. Davies and W.J. Rothwell, J. Chem. Phys. **81**, 5239 (1984).

[78] S.C. Foster, A.R.W. McKellar, and T.J. Sears, J. Chem. Phys. **81**, 578 (1984).
[79] K. Kawaguchi, C. Yamada, S. Saito, and E. Hirota, J. Chem. Phys. **82**, 1750 (1985).
[80] D.-J. Liu, S.-T. Lee, and T. Oka, J. Mol. Spectrosc. **128**, 236 (1988).
[81] J.C. Owrutsky, E.R. Keim, J.V. Coe, and R.J. Saykally, J. Phys. Chem. **93**, 5960 (1989).
[82] E.R. Keim, M.L. Polak, J.C. Owrutsky, J.V. Coe, and R.J. Saykally, J. Chem. Phys. **93**, 3111 (1990).
[83] R.J. Foltynowicz, J.D. Robinson, E.J. Zückerman, H.G. Hedderich, and E.R. Grant, J. Mol. Spectrosc. **199**, 147 (2000).
[84] H.B. Jansen and P. Ros, Chem. Phys. Lett. **3**, 140 (1969).
[85] P.J. Bruna, S.D. Peyerimhoff, and R.J. Buenker, Chem. Phys. **10**, 323 (1975).
[86] F.A. Gianturco, U.T. Lamanna, and D. Ignazzi, Chem. Phys. **48**, 387 (1980).
[87] D.J. DeFrees, J.S. Binkley, and A.D. McLean, J. Chem. Phys. **80**, 3720 (1984).
[88] N.L. Ma, B.J. Smith, and L. Radom, Chem. Phys. Lett. **197**, 573 (1992).
[89] Y. Yamaguchi, C.A. Richards Jr, and H.F. Schaefer III, J. Chem. Phys. **101**, 8945 (1994).
[90] J.M.L. Martin, P.R. Taylor, and T.J. Lee, J. Chem. Phys. **99**, 286 (1993).
[91] C. Puzzarini, R. Tarroni, P. Palmieri, S. Carter, and L. Dore, Mol. Phys. **87**, 879 (1996).
[92] M. Mladenović and S. Schmatz, J. Chem. Phys. **109**, 4456 (1998).
[93] T. van Mourik, T.H. Dunning Jr, and K.A. Peterson, J. Phys. Chem. A **104**, 2287 (2000).
[94] W.M. Vaidya, Proc. Roy. Soc. (London) A **147**, 513 (1934).
[95] D.A. Ramsay, J. Chem. Phys. **21**, 960 (1953).
[96] G. Herzberg and D.A. Ramsay, Proc. Roy. Soc. (London) A **233**, 34 (1955).
[97] B.M. Stone, M. Noble, and E.K.C. Lee, Chem. Phys. Lett. **118**, 83 (1985).
[98] K.K. Murray, T.M. Miller, D.G. Leopold, and W.C. Lineberger, J. Chem. Phys. **84**, 2520 (1986).
[99] C.B. Dane, D.R. Lander, R.F. Curl, F.K. Tittel, Y. Guo, M.I.F. Ochsner, and C.B. Moore, J. Chem. Phys. **88**, 2121 (1988).
[100] A.R.W. McKellar, J.B. Burkholder, J.J. Orlando, and C.J. Howard, J. Mol. Spectrosc. **130**, 445 (1988).
[101] G. Rumbles, E.K.C. Lee, and J.J. Valentini, J. Chem. Soc.-Faraday Trans. **86**, 3837 (1990).
[102] J.M. Brown and D.A. Ramsay, Can. J. Phys. **53**, 2232 (1975).
[103] J.W.C. Johns, A.R.W. McKellar, and M. Riggin, J. Chem. Phys. **67**, 2427 (1977).
[104] B.M. Landsberg, A.J. Merer, and T. Oka, J. Mol. Spectrosc. **67**, 459 (1977).
[105] A.D. Sappey and D.R. Crosley, J. Chem. Phys. **93**, 7601 (1990).
[106] J.P. Reilly, J.H. Clark, C.B. Moore, and G.C. Pimentel, J. Chem. Phys. **69**, 4381 (1978).
[107] J.M. Brown, J. Buttenshaw, A. Carrington, K. Dumper, and C.R. Parent, J. Mol. Spectrosc. **79**, 47 (1980).
[108] P. Botschwina, Chem. Phys. Lett. **29**, 98 (1974).
[109] K. Tanaka and E.R. Davidson, J. Chem. Phys. **70**, 2904 (1979).
[110] T.H. Dunning Jr, J. Chem. Phys. **73**, 2304 (1980).
[111] J.M. Bowman, J.S. Bittman, and L.B. Harding, J. Chem. Phys. **85**, 911 (1986).
[112] F. Pauzat, S. Chekir, and Y. Ellinger, J. Chem. Phys. **85**, 2861 (1986).
[113] D.A. Clabo Jr, W.D. Allen, R.B. Remington, Y. Yamaguchi, and H.F. Schaefer III, Chem. Phys. **123**, 187 (1988).
[114] Q. Sun, J.M. Bowman, and B. Gazdy, J. Chem. Phys. **89**, 3124 (1988).
[115] J.M. Bowman and B. Gazdy, J. Chem. Phys. **94**, 816 (1991).
[116] J.M. Bowman and B. Gazdy, Chem. Phys. Lett. **200**, 311 (1992).
[117] H. Lorenzen-Schmidt, M. Perić, and S.D. Peyerimhoff, J. Chem. Phys. **98**, 525 (1993).
[118] M. Perić, C.M. Marian, and S.D. Peyerimhoff, J. Mol. Spectrosc. **166**, 406 (1994).
[119] M. Bittererová, H. Lischka, and S. Biskupic, Int. J. Quantum Chem. **55**, 261 (1995).
[120] J. Qi, J.M. Bowman, and M.R. Manaa, J. Chem. Phys. **103**, 7664 (1995).
[121] V. Ryaboy and N. Moiseyev, J. Chem. Phys. **103**, 4061 (1995).
[122] D. Wang and J.M. Bowman, Chem. Phys. Lett. **235**, 277 (1995).
[123] H.-J. Werner, C. Bauer, P. Rosmus, H.-M. Keller, M. Stumpf, and R. Schinke, J. Chem. Phys. **102**, 3593 (1995).
[124] H.-M. Keller, H. Flöthmann, A.J. Dobbyn, R. Schinke, H.-J. Werner, C. Bauer, and P. Rosmus, J. Chem. Phys. **105**, 4983 (1996).
[125] J. Qi and J.M. Bowman, J. Chem. Phys. **105**, 9884 (1996).
[126] G.S. Whittier and J.C. Light, J. Chem. Phys. **107**, 1816 (1997).
[127] L. Serrano-Andrés, N. Forsberg, and P.-Å. Malmqvist, J. Chem. Phys. **108**, 7202 (1998).
[128] B. Poirier and J.C. Light, J. Chem. Phys. **114**, 6562 (2001).
[129] A.V. Marenich and J.E. Boggs, J. Phys. Chem. A **107**, 2343 (2003).
[130] A.V. Marenich and J.E. Boggs, J. Phys. Chem. A **108**, 5431 (2004).
[131] J.M. Brown, H.E. Radford, and T.J. Sears, J. Mol. Spectrosc. **148**, 20 (1991).
[132] E. Hirota, J. Mol. Struct **146**, 237 (1986).
[133] J.F. Ogilvie, J. Mol. Struct **31**, 407 (1976).
[134] J.A. Miller and C.T. Bowman, Progr. Energy Combustion Sci. **15**, 287 (1989).
[135] J.M. Fukuto, A.S. Dutton, and K.N. Houk, Chem. Bio. Chem. **6**, 612 (2005).

[136] J.M. Fukuto, C.H. Switzer, K.M. Miranda, and D.A. Wink, Annu. Rev. Pharmacol. Toxicol. **45**, 335 (2005).
[137] F.W. Dalby, Can. J. Phys. **36**, 1336 (1958).
[138] H.W. Brown and G.C. Pimentel, J. Chem. Phys. **29**, 883 (1958).
[139] B.L. Ulich, J.M. Hollis, and L.E. Snyder, Astrophys. J. **217**, L105 (1977).
[140] M.J.Y. Clement and D.A. Ramsay, Can. J. Phys. **39**, 205 (1961).
[141] J.L. Bancroft, J.M. Hollas, and D.A. Ramsay, Can. J. Phys. **40**, 322 (1962).
[142] P.N. Clough, B.A. Thrush, D.A. Ramsay, and J.G. Stamper, Chem. Phys. Lett. **23**, 155 (1973).
[143] M.E. Jacox and D.E. Milligan, J. Mol. Spectrosc. **48**, 536 (1973).
[144] J.W.C. Johns and A.R.W. McKellar, J. Chem. Phys. **66**, 1217 (1977).
[145] J.W.C. Johns, A.R.W. McKellar, and E. Weinberger, Can. J. Phys. **61**, 1106 (1983).
[146] J.C. Petersen and M. Vervloet, Chem. Phys. Lett. **141**, 499 (1987).
[147] S. Saito and K. Takagi, Astrophys. J **175**, L47 (1972).
[148] S. Saito and K. Takagi, J. Mol. Spectrosc. **47**, 99 (1973).
[149] A.W. Salotto and L. Burnelle, Chem. Phys. Lett. **3**, 80 (1969).
[150] P. Botschwina, Mol. Phys. **32**, 729 (1976).
[151] P. Botschwina, Chem. Phys. **40**, 33 (1979).
[152] O. Nomura and S. Iwata, Chem. Phys. Lett. **66**, 523 (1979).
[153] O. Nomura, Int. J. Quantum Chem. **18**, 143 (1980).
[154] R.N. Dixon, K.B. Jones, M. Noble, and S. Carter, Mol. Phys. **42**, 455 (1981).
[155] A. Heiberg and J. Almlöf, Chem. Phys. Lett. **85**, 542 (1982).
[156] C.E. Dateo, T.J. Lee, and D.W. Schwenke, J. Chem. Phys. **101**, 5853 (1994).
[157] R. Guadagnini, G.C. Schatz, and S.P. Walch, J. Chem. Phys. **102**, 774 (1995).
[158] D.H. Mordaunt, H. Flöthmann, M. Stumpf, H.-M. Keller, C. Beck, R. Schinke, and K. Yamashita, J. Chem. Phys. **107**, 6603 (1997).
[159] T.J. Lee, J. Chem. Phys. **99**, 9783 (1993).
[160] J. Demaison, L. Margulès, and J.E. Boggs, Chem. Phys. **260**, 65 (2000).
[161] J. Demaison, A.G. Császár, and A. Dehayem-Kamadjeu, J. Phys. Chem. A **110**, 13609 (2006).
[162] J.A. Miller, J. Chem. Phys. **84**, 6170 (1986).
[163] M.E. Summers, R.R. Conway, D.E. Siskind, M.H. Stevens, D. Offermann, M. Riese, P. Preusse, D.F. Strobel, and J.M. Russell III, Science **277**, 1967 (1997).
[164] D. Xie, C. Xu, T.-S. Ho, H. Rabitz, G. Lendvay, S.Y. Lin, and H. Guo, J. Chem. Phys. **126**, 074315 (2007).
[165] C. Yamada, Y. Endo, and E. Hirota, J. Chem. Phys. **78**, 4379 (1983).
[166] J.B. Burkholder, P.D. Hammer, C.J. Howard, J.P. Towle, and J.M. Brown, J. Mol. Spectrosc. **151**, 493 (1992).
[167] K. Nagai, Y. Endo, and E. Hirota, J. Mol. Spectrosc. **89**, 520 (1981).
[168] J.W. Buchanan, B.A. Thrush, and G.S. Tyndall, Chem. Phys. Lett. **103**, 167 (1983).
[169] J.W.C. Johns, A.R.W. McKellar, and M. Riggin, J. Chem. Phys. **68**, 3957 (1978).
[170] D.D. Nelson Jr and M.S. Zahniser, J. Mol. Spectrosc. **150**, 527 (1991).
[171] C.E. Barnes, J.M. Brown, A. Carrington, J. Pinkstone, T.J. Sears, and P.J. Thistlethwaite, J. Mol. Spectrosc. **72**, 86 (1978).
[172] C.E. Barnes, J.M. Brown, and H.E. Radford, J. Mol. Spectrosc. **84**, 179 (1980).
[173] S.P. Walch and R.J. Duchovic, J. Chem. Phys. **94**, 7068 (1991).
[174] C. Xu, D. Xie, D.H. Zhang, S.Y. Lin, and H. Guo, J. Chem. Phys. **122**, 244305 (2005).
[175] C. Lanczos, J. Res. Natl. Bur. Stand. **45**, 255 (1950).
[176] C. Xu, B. Jiang, D. Xie, S.C. Farantos, S.Y. Lin, and H. Guo, J. Phys. Chem. A **111**, 10353 (2007).
[177] S.Y. Lin, H. Guo, P. Honvault, C. Xu, and D. Xie, J. Chem. Phys. **128**, 014303 (2008).
[178] C.F. Melius and R.J. Blint, Chem. Phys. Lett. **64**, 183 (1979).
[179] A. Komornicki and R.L. Jaffe, J. Chem. Phys. **71**, 2150 (1979).
[180] M.R. Pastrana, L.A.M. Quintales, J. Brãndao, and A.J.C. Varandas, J. Phys. Chem. **94**, 8073 (1990).
[181] P.R. Bunker, I.P. Hamilton, and P. Jensen, J. Mol. Spectrosc. **155**, 44 (1992).
[182] V. Barone, J. Chem. Phys. **101**, 10666 (1994).
[183] V.J. Barclay and I.P. Hamilton, J. Chem. Phys. **103**, 2834 (1995).
[184] V.A. Mandelshtam, T.P. Grozdanov, and H.S. Taylor, J. Chem. Phys. **103**, 10074 (1995).
[185] P. Botschwina and M. Horn, J. Mol. Spectrosc. **181**, 452 (1997).
[186] P. Jensen, R.J. Buenker, J.-P. Gu, G. Osmann, and P.R. Bunker, Can. J. Phys. **79**, 641 (2001).
[187] J. Troe and V.G. Ushakov, Chem. Phys. **346**, 186 (2008).
[188] J. Troe and V.G. Ushakov, Chem. Phys. **346**, 193 (2008).
[189] J.M. Oakes, L.B. Harding, and G.B. Ellison, J. Chem. Phys. **83**, 5400 (1985).
[190] M. Horn, S. Seeger, R. Oswald, and P. Botschwina, Z. Phys. D: At., Mol. Clusters **36**, 293 (1996).
[191] W.-T. Chan and I.P. Hamilton, J. Chem. Phys. **105**, 5907 (1996).
[192] G.J. Vazquez, R.J. Buenker, and S.D. Peyerimhoff, J. Chem. Phys. **90**, 7229 (1989).
[193] J. Liang and H. Li, J. Electron Spectrosc. Relat. Phenom. **135**, 119 (2004).
[194] R. Li, X. Zhang, H. Zheng, J. Liang, and Z. Cui, J. Mol. Struct. **860**, 106 (2008).

[195] M.W. Crofton, M.-F. Jagod, B.D. Rehfuss, W.A. Kreiner, and T. Oka, J. Chem. Phys. **88**, 666 (1988).
[196] M.W. Crofton, W.A. Kreiner, M.-F. Jagod, B.D. Rehfuss, and T. Oka, J. Chem. Phys. **83**, 3702 (1985).
[197] M.-F. Jagod, C.M. Gabrys, M. Rösslein, D. Uy, and T. Oka, Can. J. Phys. **72**, 1192 (1994).
[198] J. Dyke, N. Jonathan, E. Lee, and A. Morris, J. Chem. Soc., Faraday Trans. **2 72**, 1385 (1976).
[199] T. Koenig, T. Balle, and J.C. Chang, Spectrosc. Lett. **9**, 755 (1976).
[200] T. Koenig, T. Balle, and W. Snell, J. Am. Chem. Soc. **97**, 662 (1975).
[201] X. Liu, R.L. Gross, and A.G. Suits, Science **294**, 2527 (2001).
[202] W.A. Lathan, W.J. Hehre, L.A. Curtiss, and J.A. Pople, J. Am. Chem. Soc. **93**, 6377 (1971).
[203] G.T. Surratt and W.A. Goddard III, Chem. Phys. **23**, 39 (1977).
[204] F.T. Chau, J. Mol. Struct. **119**, 281 (1985).
[205] D.J. DeFrees and A.D. McLean, J. Chem. Phys. **82**, 333 (1985).
[206] W.P. Kraemer and V. Špirko, J. Mol. Spectrosc. **149**, 235 (1991).
[207] P. Pracna, V. Špirko, and W.P. Kraemer, J. Mol. Spectrosc. **158**, 433 (1993).
[208] H.-G. Yu and T.J. Sears, J. Chem. Phys. **117**, 666 (2002).
[209] A. Halkier, T. Helgaker, P. Jørgensen, W. Klopper, H. Koch, J. Olsen, and A.K. Wilson, Chem. Phys. Lett. **286**, 243 (1998).
[210] C. Yamada, E. Hirota, and K. Kawaguchi, J. Chem. Phys. **75**, 5256 (1981).
[211] P.L. Holt, K.E. McCurdy, R.B. Weisman, J.S. Adams, and P.S. Engel, J. Chem. Phys. **81**, 3349 (1984).
[212] P.B. Kelly and S.G. Westre, Chem. Phys. Lett. **151**, 253 (1988).
[213] N.E. Triggs, M. Zahedi, J.W. Nibler, P. DeBarber, and J.J. Valentini, J. Chem. Phys. **96**, 1822 (1992).
[214] M. Zahedi, J.A. Harrison, and J.W. Nibler, J. Chem. Phys. **100**, 4043 (1994).
[215] S. Hädrich, S. Hefter, B. Pfelzer, T. Doerk, P. Jauernik, and J. Uhlenbusch, Chem. Phys. Lett. **256**, 83 (1996).
[216] L.Y. Tan, A.M. Winer, and G.C. Pimentel, J. Chem. Phys. **57**, 4028 (1972).
[217] J. Wormhoudt and K.E. McCurdy, Chem. Phys. Lett. **156**, 47 (1989).
[218] T. Amano, P.F. Bernath, C. Yamada, Y. Endo, and E. Hirota, J. Chem. Phys. **77**, 5284 (1982).
[219] I. Tanarro, M.M. Sanz, D. Bermejo, C. Domingo, and J. Santos, J. Chem. Phys. **100**, 238 (1994).
[220] I. Tanarro, M.M. Sanz, C. Domingo, D. Bermejo, J. Santos, and J.L. Domenech, J. Phys. Chem. **98**, 5862 (1994).
[221] G.A. Bethardy and R.G. Macdonald, J. Chem. Phys. **103**, 2863 (1995).
[222] S. Davis, D.T. Anderson, G. Duxbury, and D.J. Nesbitt, J. Chem. Phys. **107**, 5661 (1997).
[223] K. Kawaguchi, Can. J. Phys. **79**, 449 (2001).
[224] A. Snelson, J. Phys. Chem. **74**, 537 (1970).
[225] M.E. Jacox, J. Mol. Spectrosc. **66**, 272 (1977).
[226] T. Momose, M. Miki, M. Uchida, T. Shimizu, I. Yoshizawa, and T. Shida, J. Chem. Phys. **103**, 1400 (1995).
[227] S. Tam, M. Macler, and M.E. Fajardo, J. Chem. Phys. **106**, 8955 (1997).
[228] D.S. Marynick and D.A. Dixon, Proc. Natl. Acad. Sci. USA **74**, 410 (1977).
[229] K. Raghavachari, R.A. Whiteside, J.A. Pople, and P.v.R. Schleyer, J. Am. Chem. Soc. **103**, 5649 (1981).
[230] V. Špirko and P.R. Bunker, J. Mol. Spectrosc. **95**, 381 (1982).
[231] P. Botschwina, J. Flesch, and W. Meyer, Chem. Phys. **74**, 321 (1983).
[232] D.M. Chipman, J. Chem. Phys. **78**, 3112 (1983).
[233] F.T. Chau, J. Electron Spectrosc. Relat. Phenom. **40**, 59 (1986).
[234] U. Salzner and P.v.R. Schleyer, Chem. Phys. Lett. **199**, 267 (1992).
[235] D.A. Dixon, D. Feller, and K.A. Peterson, J. Phys. Chem. A **101**, 9405 (1997).
[236] O. Roberto-Neto, S. Chakravorty, and F.B.C. Machado, Int. J. Quantum Chem. **103**, 649 (2005).
[237] J. Burdett, J. Chem. Phys. **52**, 2983 (1970).