The Journal of Chemical Physics

The *trans*-HOCO radical: Quartic force fields, vibrational frequencies, and spectroscopic constants

Cite as: J. Chem. Phys. **135**, 134301 (2011); https://doi.org/10.1063/1.3643336
Submitted: 01 August 2011 . Accepted: 05 September 2011 . Published Online: 03 October 2011

Ryan C. Fortenberry, Xinchuan Huang, Joseph S. Francisco, T. Daniel Crawford, and Timothy J. Lee

View Online

Export Citation

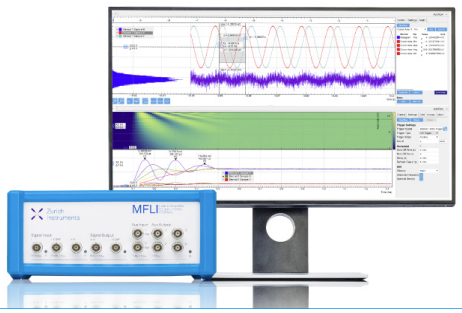
ARTICLES YOU MAY BE INTERESTED IN

Vibrational frequencies and spectroscopic constants from quartic force fields for cis-HOCO: The radical and the anion
The Journal of Chemical Physics **135**, 214303 (2011); https://doi.org/10.1063/1.3663615

Quartic force field predictions of the fundamental vibrational frequencies and spectroscopic constants of the cations $HOCO^+$ and $DOCO^+$
The Journal of Chemical Physics **136**, 234309 (2012); https://doi.org/10.1063/1.4729309

Vibrational calculation for the HOCO radical and the cis-HOCO anion
The Journal of Chemical Physics **137**, 014306 (2012); https://doi.org/10.1063/1.4732150

Challenge us.
What are your needs for periodic signal detection?
Zurich Instruments
Watch



© 2011 American Institute of Physics.

The *trans*-HOCO radical: Quartic force fields, vibrational frequencies, and spectroscopic constants

Ryan C. Fortenberry,[1] Xinchuan Huang,[2,a)] Joseph S. Francisco,[3] T. Daniel Crawford,[1,b)] and Timothy J. Lee[4,c)]
[1]*Department of Chemistry, Virginia Tech, Blacksburg, Virginia 24061, USA*
[2]*SETI Institute, 189 Bernardo Avenue, Suite 100, Mountain View, California 94043, USA*
[3]*Department of Chemistry, Purdue University, West Lafayette, Indiana 47907, USA*
[4]*NASA Ames Research Center, Moffett Field, California 94035-1000, USA*

(Received 1 August 2011; accepted 5 September 2011; published online 3 October 2011)

In the search for a full mechanism creating CO_2 from OH + CO, it has been suggested that creation of the hydroxyformyl or HOCO radical may be a necessary step. This reaction and its transient intermediate may also be responsible for the regeneration of CO_2 in such high quantities in the atmosphere of Mars. Past spectroscopic observations of this radical have been limited and a full gas phase set of the fundamental vibrational frequencies of the HOCO radical has not been reported. Using established, highly accurate quantum chemical coupled cluster techniques and quartic force fields, we are able to compute all six fundamental vibrational frequencies and other spectroscopic constants for *trans*-HOCO in the gas phase. These methods have yielded rotational constants that are within 0.01 cm^{-1} for A_0 and 10^{-4} cm^{-1} for B_0 and C_0 compared with experiment as well as fundamental vibrational frequencies within 4 cm^{-1} of the known gas phase experimental ν_1 and ν_2 modes. Such results lead us to conclude that our prediction of the other four fundamental modes of *trans*-HOCO are also quite reliable for comparison to future experimental observation, though the discrepancy for the torsional mode may be larger since it is fairly anharmonic. With the upcoming European Space Agency/NASA ExoMars Trace Gas Orbiter, these data may help to establish whether HOCO is present in the Martian sky and what role it may play in the retention of a CO_2-rich atmosphere. Furthermore, these data may also help to clear up questions built around the fundamental chemical process of how exactly the OH + CO reaction progresses. © *2011 American Institute of Physics*. [doi:10.1063/1.3643336]

I. INTRODUCTION

Creation of the hydroxyformyl (HOCO) radical has been proposed as a necessary intermediate step in the reaction of OH + CO.[1,2] This reaction is known ultimately to produce carbon dioxide as well as help to retain carbon monoxide in Earth's atmosphere,[3,4] but the full gas phase mechanism of how CO_2 forms from this reaction has not been elucidated as of yet (see Ref. 5 for a full discussion). Considering other planetary bodies, the atmosphere of Mars is nearly synonymous with CO_2. The red planet's atmosphere is over 95% CO_2 (Ref. 6), but the mechanism for the atmospheric creation, retention, and stability of such a high concentration of atmospheric CO_2 on Mars is also not currently fully resolved[7,8] although surface adsorption models such as the Mars-van Krevelen reaction show some promise in that area.[9] If HOCO is vital to the creation of CO_2 in Earth's atmosphere, such may also be the case, and to a much greater degree, on the fourth planet from the sun.

The upcoming European Space Agency/NASA ExoMars Trace Gas Orbiter mission will be able to use its infrared instruments to detect, as its name suggests, minuscule amounts of gases within the Martian atmosphere. The most notable of these is certainly methane which is an indicator of past or potentially even present forms of life as we know it.[10] However, other molecules should be detected in low but measurable abundances, and these may be necessary for the creation of methane or the regeneration of CO_2. Hence, there exists the need to have reference data for HOCO so that its presence in the Martian atmosphere can be determined. The detection of HOCO would yield a greater understanding of the mechanism that regenerates CO_2. Unfortunately, little conclusive gas phase IR data for the HOCO radical exists. The ν_1 O−H stretch and ν_2 C=O stretch have been measured experimentally in the gas phase at 3635.702 cm^{-1} (Ref. 11) and 1852.567 cm^{-1} (Ref. 12), respectively, for *trans*-HOCO, the most stable conformer. However, all other known frequencies for both *cis*-HOCO and the other four fundamentals of *trans*-HOCO have only been measured in the condensed phase trapped in matrices of Ar, Ne, and CO.[1,13,14] Other theoretical work also has not yet proven to be beneficial in accurately predicting the gas phase fundamental frequencies of either isomer.[15]

Recently, theoretical chemistry has proven to be of vital significance in the prediction of spectroscopic properties necessary for the detection of interstellar molecular species. Botschwina and Oswald[16] built on previous work by Aoki[17] to generate highly accurate spectroscopic data

a)Electronic mail: Xinchuan.Huang-1@nasa.gov.
b)Electronic mail: crawdad@vt.edu.
c)Electronic mail: Timothy.J.Lee@nasa.gov.

 © 2011 American Institute of Physics

for the microwave-range detection of C_5N^- by Cernicharo and co-workers[18] where corresponding laboratory data were not available. Further, computational tools have been utilized by Yu, Francisco, and co-workers[19–32] to better characterize the HOCO formation process, but there is still much that is uncertain, including accurate rovibrational spectroscopic constants and several of the fundamental vibrational frequencies. Huang, Lee, and co-workers[33–37] have predicted the fundamental vibrational frequencies of various molecular species to within a few cm^{-1} using advanced quantum chemical approaches which, further demonstrate the potential role of quantum chemistry in accurately examining difficult molecules often found in the conditions of interstellar space and extraterrestrial atmospheres. Additionally, Crawford and co-workers[38–42] have highlighted the need for highly accurate coupled cluster methods to examine radicals of this size. Hence, using techniques similar to those developed by Lee *et al.*,[33–37,43–45] we have examined the gas phase vibrational frequencies of the *trans*-HOCO radical using high accuracy coupled cluster quartic force fields (QFFs) in order to generate reference data for atmospheric and planetary measurements.

The paper is organized as follows: Section II includes a discussion of the computational approaches and methods used for the analysis of the fundamental frequencies and spectroscopic properties of *trans*-HOCO; this is followed by a discussion of the results obtained in this study; and we conclude with a summary of our findings and acknowledgements.

II. COMPUTATIONAL DETAILS

Using restricted open-shell Hartree–Fock (ROHF) (Ref. 46) as the reference wavefunction with the coupled cluster singles, doubles, and perturbative triples method[47] [CCSD(T)] combined with Dunning's correlation-consistent cc-pV5Z basis set[48,49] a minimum energy geometry was obtained that was further corrected for core-correlation effects using a basis set specifically derived for such adjustments by Martin and Taylor (MT).[50] We shall refer to this basis set as the MT basis set. From this reference geometry a quartic force field was generated from step lengths of 0.005 Å and 0.005 rad. For HOCO, a tetra-atomic radical with C_s symmetry, 743 symmetry unique geometries, out of 805 in total, were generated to compute all required force constants in the quartic force field. The simple internal coordinates used in the quartic force field determination are, from Fig. 1: (1) the C=O_2 bond length, (2) the C−O_1 bond length, (3) the O_1−H bond length, (4) the O_2−C−O_1 bond angle, (5) the C−O_1−H bond angle, and (6) the torsional motion of all four atoms.

At each of the 743 points, ROHF-CCSD(T) single-point energies were computed with Dunning's correlation consistent basis sets but augmented with diffuse functions[48,51] necessary to treat a radical, aug-cc-pVXZ (where X = T, Q, and 5). A three-point formula[52] utilized previously[33–37] was employed to obtain energies extrapolated to the one-particle complete basis set (CBS) limit. To this CCSD(T)/CBS energy at each point, core-correlation corrections computed from the aforementioned MT core-correlating basis set, scalar relativistic terms (aTZ-DK),[53,54] and higher-order electron correlation effects using the cc-pVTZ basis set with the full CCSDT method[55,56] implemented in the CFOUR (Ref. 57) quantum chemical program were combined to give a composite energy represented as

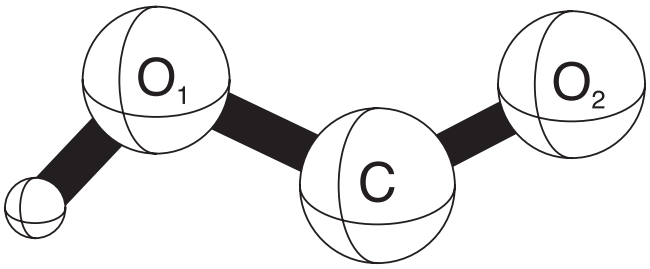


FIG. 1. The equilibrium geometry computed from the CcCRE QFF.

$$E_{tot} = E_{\text{aTQ5}\rightarrow\text{CBS}} + (E_{\text{MT,core}} - E_{\text{MT}}) + (E_{\text{aTZ-DK,rel.}} - E_{\text{aTZ-DK}}) + (E_{\text{CCSDT/TZ}} - E_{\text{CCSD(T)/TZ}}). \quad (1)$$

The inclusion of the core-correlation, scalar relativistic, and the higher-order electron correlation terms should represent the most accurate exclusively coupled cluster QFF used to date for the prediction of vibrational frequencies and related spectroscopic constants. Using the equilibrium geometry as an example, these corrections represent a stabilization to the estimated CBS energy of 450.6 kJ/mol for the core correlation, 337.3 kJ/mol for the scalar relativistic term, and 0.5 kJ/mol for the higher-order electron correlation energy. However, it is the behavior of these corrections at each point and not their individual absolute magnitudes that affects the QFF's performance. Besides those computations involving CCSDT and its subtracted CCSD(T) counterpart, all computations utilized the MOLPRO 2010.1 program.[58] The ROHF reference is the same (Ref. 46) for both programs, but the definition of the core orbitals differs slightly between the two packages. This difference is negligible, however, since the sum of the residual squares in fitting the QFF is on the order of 10^{-16}.

From these points and their corresponding CBS + core correlation + scalar relativistic + higher-order electron correlation (CcCRE) composite energies, the simple internal force constants and the "actual" minimum (which slightly deviates from the reference geometry) were derived from the fitting of the QFF where, again, the sum of the residuals squared is acceptably small as mentioned above. The INTDER program[59] computed the Cartesian derivatives from the force constants. These were fed into the SPECTRO (Ref. 60) program for the second-order vibrational perturbation theory (VPT) (Refs. 61–63) treatments. Additionally, the simple internal QFF was converted to Morse-Cosine coordinates[44] which makes use of periodic functions for each non-stretching mode. These coordinates were used to determine the variationally computed frequencies using the vibrational configuration interaction (VCI) method with the MULTIMODE program.[64,65] Furthermore, other QFFs were also tested. These included the CcCR QFF where the higher-order electron correlation correction has been excluded and the CR QFF which only contains the first and third terms of Eq. (1).

III. RESULTS

The CcCRE QFF zero-point and equilibrium structures for $X\ ^2A'$ *trans*-HOCO are shown in Fig. 1. The bond lengths, bond angles, rotational constants, and associated harmonic vibrational frequencies are given in Table I where the equilibrium structure is the result of the "position averaged" values (synonymous with the r_z values) from the VPT2 results. Oyama and co-workers[66] used UCCSD(T)-F12/aug-cc-pVTZ computations to report geometry parameters for *trans*-HOCO as part of a larger study on the rotational transitions of *cis*- and *trans*-HOCO and DOCO derived from Fourier-transformed microwave (FTMW) spectroscopy. The UCCSD(T)-F12/aug-cc-pVTZ equilibrium geometry, also in Table I, does not vary much as compared to our CcCRE QFF equilibrium geometry: 0.001 Å for the bond lengths and 0.1° for the bond angles. Additionally, RCCSD(T)/cc-pCV5Z computations by Botschwina,[67] also listed in Table I, give geometry values that are even closer to our CcCRE QFF results than UCCSD(T)-F12/aug-cc-pVTZ.

Oyama and co-workers' experimental FTMW zero-point geometry was reported to be in good agreement with their computed equilibrium geometry (within 0.01 Å for bond lengths and 0.4° bond angles) and, subsequently, in good agreement with the geometry computed by Botschwina[67] rendering our CcCRE QFF geometry quite accurate, as well. The FTMW zero-point rotational constants of 5.59614, 0.38137, and 0.35647 cm^{-1} (or 167 768.064, 11 433.322, and 10 686.63 MHz) correlate nearly exactly (within 0.002 cm^{-1}) with a previous millimeter-wave experiment done by Radford, Wei, and Sears[68] and are in very good agreement with Botschwina's RCCSD(T)/cc-pCV5Z equilibrium rotational constants.[67] The latter of which are nearly identical to our CcCRE QFF equilibrium rotational constants (see Table I). Additionally, our CcCRE QFF zero-point rotational constants are very close to those observed in the FTMW experiment reported by Oyama and co-workers:[66] within 0.02 cm^{-1} for A_0 and 5×10^{-4} cm^{-1} for B_0 and C_0. Furthermore, UCCSD(T)/aug-cc-pVDZ harmonic vibrational frequencies, listed in the bottom of Table I, computed by Feller, Dixon, and Francisco[69] are comparable to the CcCRE QFF harmonic frequencies. Such corroborating evidence indicates that our lowest energy structure of *trans*-HOCO derived from the fitting of the CcCRE QFF is reliable. Additionally, another QFF, the CR QFF which only includes the CBS-extrapolated electronic energy and the scalar relativistic terms from Eq. (1), predicts vibrationally averaged rotational constants of 5.58209, 0.38054, and 0.35570 cm^{-1}. These CR QFF rotational constants deviate from the FTMW experimental results by about the same amount as the CcCRE results, but these A_0, B_0, and C_0 values are smaller than the experimental values whereas the CcCRE constants are all larger than experiment.

The associated anharmonic frequencies for the CcCRE QFF of *trans*-HOCO are given in Table II while the anharmonic constants are given in Table III. Vibration-rotation interaction constants and quartic and sextic centrifugal distortion constants are compiled in Table IV and Table V contains the quadratic, cubic, and quartic force constants. All spectroscopic constants were computed with second-order vibrational perturbation theory via SPECTRO and should be useful in the analysis of high-resolution experiments or astronomical observations. The VPT computations require the explicit inclusion of a fourfold Fermi resonance polyad[45] involving ν_3, ν_4, $2\nu_5$, and $2\nu_6$. A type 2 Fermi resonance is necessary for $\nu_5 = \nu_4 + \nu_2$. Lastly, a Coriolis resonance between ν_6 and ν_5 is also present.

TABLE I. Minimum structure, rotational constants, and harmonic frequencies for HOCO.[a]

Zero-point			Equilibrium			
	This work	Expt.[b]		This work	Oyama *et al.*[c]	Botschwina[d]
R(O_1−H)	0.957 73 Å	0.974 Å	R(O_1−H)	0.961 27 Å	0.963 Å	0.9617 Å
R(C−O_1)	1.348 50 Å	1.342 Å	R(C−O_1)	1.339 20 Å	1.342 Å	1.3391 Å
R(C−O_2)	1.178 12 Å	1.181 Å	R(C−O_2)	1.175 18 Å	1.178 Å	1.1754 Å
∠H−O_1−C	108.139°	107.4°	∠H−O_1−C	107.993°	107.8°	107.95°
∠O_1−C−O_2	126.949°	127.4°	∠O_1−C−O_2	126.981°	127.0°	127.15°
A_0	5.612 76 cm^{-1}	5.596 14 cm^{-1}	A_e	5.586 21 cm^{-1}	...	5.595 5 cm^{-1}
B_0	0.381 88 cm^{-1}	0.381 37 cm^{-1}	B_e	0.384 79 cm^{-1}	...	0.383 97 cm^{-1}
C_0	0.356 98 cm^{-1}	0.356 47 cm^{-1}	C_e	0.360 00 cm^{-1}	...	0.359 28 cm^{-1}
			Freq (in cm^{-1})			
	Mode	Description	This work	Previous work[e]		
	ω_1	a′ O_1−H stretch	3833.9	3781.0		
	ω_2	a′ C=O_2 stretch	1903.5	1848.0		
	ω_3	a′ H−O_1−C bend	1261.1	1250.9		
	ω_4	a′ C−O_1 stretch	1090.1	1036.3		
	ω_5	a′ O_1−C−O_2 bend	624.2	596.5		
	ω_6	a″ torsional mode	537.0	523.2		

[a]The minimum structure and harmonic vibrational frequencies are computed from the CcCRE QFF.
[b]Fourier-transformed microwave results from Ref. 66.
[c]UCCSD(T)-F12/aug-cc-pVTZ results from Ref. 66.
[d]RCCSD(T)/cc-pCV5Z results Ref. 67.
[e]UCCSD(T)/aug-cc-pVDZ results from Ref. 69.

TABLE II. Fundamental vibrational frequencies (cm^{-1}) for *trans*-HOCO from VPT and VCI-s and VCI-l 5MR computations for the CcCRE QFF, VPT and VCI-l for the CcCR QFF, VPT and VCI-l for the CR QFF, and both condensed and gas phase experimental results.

		CcCRE			CcCR		CR		Expt.	
Mode	Description	VPT	5MR-s	5MR-l	VPT	5MR-l	VPT	5MR-l	Condensed[a]	Gas phase[b]
ν_1	a′ O_1-H stretch	3642.0	3652.6	3640.5	3640.7	3634.4	3636.0	3632.9	3628.0	3635.702
ν_2	a′ $C=O_2$ stretch	1861.0	1861.5	1861.1	1862.2	1862.2	1855.8	1856.0	1848.0	1852.567
ν_3	a′ $H-O_1-C$ bend	1217.3	1221.3	1218.0	1213.7	1214.2	1215.9	1218.9	1211.2	
ν_4	a′ $C-O_1$ stretch	1053.0	1042.9	1052.8	1053.0	1052.8	1048.2	1048.2	1050.4	
ν_5	a′ O_1-C-O_2 bend	617.3	618.4	617.5	616.6	616.9	614.5	615.9	615	
ν_6	a″ torsional mode	501.2	511.2	488.6	497.5	484.6	501.8	492.1	508.1	
ZPE		4560.9	4555.1	4551.4	4559.2	4549.8	4549.9	4546.2		

[a]Condensed phase data from Jacox and co-workers (Refs. 1, 13, and 14).
[b]Gas phase data from Petty and Moore (Ref. 11) for ν_1 and Sears, Fawzy, and Johnson (Ref. 12) for ν_2.

The anharmonic vibrational frequencies, again from Table II, include both the VPT and variationally computed VCI frequencies. For the variational frequencies, four-mode and five-mode representations for the coupling configuration interaction computations (4MR and 5MR, respectively) are both shown. The different numbers of modes refer to the number of modes allowed to couple within the expansion formula defined[65] as

$$V(Q_1, Q_2, \ldots, Q_N) = \sum_i V_i^{(1)}(Q_i) + \sum_{ij} V_{ij}^{(2)}(Q_i, Q_j) + \cdots + \sum_{ijk\ldots N} V_{ijk\ldots N}^{(N)}(Q_i, Q_j, Q_k, \ldots, Q_N), \quad (2)$$

where N is the number of modes for each expansion level; $N = 6$ is the largest expansion level for the HOCO radical since there are six total degrees of freedom. 4MR and 5MR are truncations at the $N = 4$ and $N = 5$ levels, respectively. The $V_i^{(1)}$ term is the one-mode potential for the ith mode at a given geometry, $V_{ij}^{(2)}$ is the two-mode potential for the corresponding ith and jth modes, and so on for $V_{ijk}^{(3)}$ and larger up to $V_{ijk\ldots N}^{(N)}$. The Q_i terms from Eq. (2) are simply the coordinates of a given normal mode i.

Initial VCI computations of the fundamental vibrational frequencies used a small but reasonable set of vibrational variational basis functions to describe the vibrational behavior of *trans*-HOCO. The CI matrices, one of which is composed of a′ functions while the other a″ functions, contain 2738 a′ functions and 1399 a″ functions for the 4MR computations. The 5MR CI matrices contain 3064 and 1829, respectively. These 4MR and 5MR computations both require 30 Gaussian integration points, 25 primitive harmonic oscillator basis functions contracted down to 10 basis functions for each mode, and 16 HEG (the abbreviation for Gauss-Hermite) quadrature points. Since the 4MR and 5MR frequencies differ by less than 0.2 cm^{-1}, it is clear that convergence of the mode coupling levels in the VCI method has been achieved. Additionally, since the 4MR and 5MR computations are nearly identical, only the 5MR results will be included in this discussion and will be referred to as 5MR-s or simply VCI-s, the "s" for small.

TABLE III. Anharmonic constant matrix for the CcCRE QFF (in cm^{-1}).

Mode	1	2	3	4	5	6
1	−85.526					
2	−3.611	−13.089				
3	−19.889	−5.572	−11.488			
4	−4.952	−15.134	−9.976	−8.733		
5	−2.273	−6.564	−1.549	−7.134	−0.131	
6	−10.902	−1.705	−2.869	−5.509	4.337	−13.768

However, the level of agreement between the VPT and VCI-s frequencies is not consistent, especially for ν_6, the torsional mode. Strong agreement (i.e., <1 cm^{-1}) is present between the two methods for the ν_2 and ν_5 modes, and fairly good agreement exists for the ν_3 mode for which the difference is about 4 cm^{-1}. The $C-O_1$ stretch, ν_4, differs between VPT and VCI by 10.1 cm^{-1}, and the $H-O_1$ stretch, ν_1, differs by around the same value. The torsional motion, ν_6, has a discrepancy, again, of about 10 cm^{-1} between VPT (501.2 cm^{-1}) and VCI-s (511.2 cm^{-1}). However, the VCI-s computation predicts the energy of this particular mode to be higher than the VPT which was not expected based on previous work.

Even though direct comparison between the experimental condensed phase vibrational frequencies and the CcCRE QFF simulated gas phase frequencies is not a perfectly direct comparison as the use of gas phase experimental data would be, it was still noticed that VCI-s appears to overcorrect the ν_4 vibrational frequency of 1042.9 cm^{-1} even when compared to the condensed phase result of 1050.4 cm^{-1}. For ν_1 and ν_2, where gas phase experimental data are known, the condensed phase experimental frequencies are a few wavenumbers lower in energy than the gas phase, and an inference of a similar relationship to the other four modes is thermodynamically reasonable but certainly not guaranteed. The potential overcorrection of ν_4 and the difference in frequency between our results and the condensed and gas phase experimental data by 10 cm^{-1} or so for ν_1, ν_4, and ν_6 indicated that a reanalysis of the VCI computations was necessary.

The subsequent action was the use of a substantially larger set of basis functions for describing the fundamental vibrational frequencies using VCI. We will call this computation VCI-l for the use of a larger set of harmonic oscillator basis functions. 4MR-l utilizes CI matrices composed of 19 305 a′ functions and 10 820 a″ functions, while the

TABLE IV. CcCRE QFF computed vibration-rotation interaction constants and quartic and sextic centrifugal distortion constants of *trans*-HOCO.

Vib-rot constants (MHz)				Distortion constants				Watson *S* reduction			
Mode	α^A	α^B	α^C	(MHz)		(Hz)		(MHz)		(Hz)	
1	1308.8	10.9	14.2	τ'_{aaaa}	−87.735	Φ_{aaa}	8391.870	D_J	0.009	H_J	0.009
2	1444.7	45.3	42.0	τ'_{bbbb}	−0.043	Φ_{bbb}	0.017	D_{JK}	−0.293	H_{JK}	−1.222
3	−3100.0	5.4	19.4	τ'_{cccc}	−0.028	Φ_{ccc}	0.001	D_K	22.219	H_{KJ}	−140.003
4	−597.6	84.8	87.7	τ'_{aabb}	0.630	Φ_{aab}	−69.672	d_1	−0.001	H_K	8533.087
5	−2972.8	−4.3	15.1	τ'_{aacc}	0.474	Φ_{abb}	−0.848	d_2	0.000	h_1	0.004
6	2324.8	32.7	2.0	τ'_{bbcc}	−0.034	Φ_{aac}	−72.789			h_2	0.000
						Φ_{bbc}	0.012			h_3	0.000
						Φ_{acc}	−0.045				
						Φ_{bcc}	0.006				
						Φ_{abc}	−1.972				

corresponding 5MR-l computation utilizes matrices of 21 604 and 14 146 functions, respectively. Additionally, these larger VCI-l computations require 36 Gaussian integration points, 31 primitive basis functions contracted down to 15 on each mode, and 20 HEG quadrature points. Again, the 4MR-l results have been excluded since they differ from the 5MR-l results by less than 0.02 cm^{-1}, and the 5MR-l frequencies are, again, synonymous with the VCI-l frequencies.

Table II clearly shows a substantial increase in agreement between VPT and VCI when using VCI-l with its larger number of basis functions. The ν_2, ν_3, ν_4, and ν_5 frequencies are nearly identical (i.e., <1 cm^{-1}) between VCI-l and VPT, and the VCI-l 3640.5 cm^{-1} ν_1 mode is only 1.5 cm^{-1} lower in energy than the corresponding 3642.0 cm^{-1} VPT result. Interestingly, ν_6 for VCI-l (488.6 cm^{-1}) is at nearly the same level of agreement with VPT as VCI-s (around 10 cm^{-1}), but the VPT frequency of 501.6 cm^{-1} is now higher than its VCI-l counterpart. Inclusion of the additional basis functions also places the VCI-l ν_4 mode above the condensed phase experimental result of 1050.4 cm^{-1}. This shift to a higher frequency for ν_4 is actually the result of a state crossing. The use of more basis functions in the computation shows that the dominant character of the VCI-s ν_4 state is better described as the $2\nu_1$ state in VCI-l while the VCI-s $2\nu_1$ is really the

TABLE V. Quadratic, cubic, and quartic force constants (in mdyn/Å^n · rad^m) for the HOCO radical in the simple-internal coordinate system for the CcCRE QFF.

F_{11}	14.596 327	F_{431}	−0.1313	F_{1111}	593.25	F_{4432}	0.15	F_{5531}	0.25
F_{21}	1.472 200	F_{432}	−0.2134	F_{2111}	7.85	F_{4433}	−0.39	F_{5532}	0.88
F_{22}	5.807 740	F_{433}	0.0719	F_{2211}	−1.02	F_{4441}	2.77	F_{5533}	−0.47
F_{31}	−0.079 973	F_{441}	−1.7839	F_{2221}	8.34	F_{4442}	3.97	F_{5541}	0.19
F_{32}	0.012 893	F_{442}	−1.7691	F_{2222}	236.37	F_{4443}	0.27	F_{5542}	0.34
F_{33}	8.220 563	F_{443}	−0.0883	F_{3111}	1.18	F_{4444}	3.91	F_{5543}	−0.04
F_{41}	0.401 357	F_{444}	−1.4840	F_{3211}	0.17	F_{5111}	0.17	F_{5544}	0.38
F_{42}	0.441 020	F_{511}	−0.0590	F_{3221}	−0.72	F_{5211}	−0.56	F_{5551}	0.04
F_{43}	0.067 552	F_{521}	0.1178	F_{3222}	4.26	F_{5221}	0.11	F_{5552}	0.04
F_{44}	1.362 958	F_{522}	−1.1302	F_{3311}	−0.27	F_{5222}	−0.01	F_{5553}	1.21
F_{51}	0.052 311	F_{531}	−0.0163	F_{3321}	0.30	F_{5311}	−0.13	F_{5554}	−0.15
F_{52}	0.431 362	F_{532}	−0.5147	F_{3322}	−1.08	F_{5321}	0.42	F_{5555}	−0.97
F_{53}	0.183 414	F_{533}	−0.0194	F_{3331}	−0.20	F_{5322}	0.27	F_{6611}	−0.13
F_{54}	0.146 008	F_{541}	−0.1797	F_{3332}	−0.79	F_{5331}	−0.31	F_{6621}	0.06
F_{55}	0.762 089	F_{542}	0.0918	F_{3333}	357.19	F_{5332}	0.33	F_{6622}	0.40
F_{66}	0.116 757	F_{543}	−0.0288	F_{4111}	2.86	F_{5333}	−1.88	F_{6631}	0.06
F_{111}	−103.8339	F_{544}	0.0186	F_{4211}	2.69	F_{5411}	−0.13	F_{6632}	−0.08
F_{211}	−3.6315	F_{551}	−0.0637	F_{4221}	4.49	F_{5421}	0.24	F_{6633}	−0.00
F_{221}	−1.0468	F_{552}	−0.7192	F_{4222}	0.48	F_{5422}	−0.96	F_{6641}	0.02
F_{222}	−44.3548	F_{553}	−0.3739	F_{4311}	−0.10	F_{5431}	0.01	F_{6642}	0.24
F_{311}	−0.1141	F_{554}	−0.2112	F_{4321}	0.41	F_{5432}	0.08	F_{6643}	−0.08
F_{321}	0.1800	F_{555}	−0.9620	F_{4322}	0.36	F_{5433}	0.02	F_{6644}	0.27
F_{322}	−0.9188	F_{661}	−0.0173	F_{4331}	−0.05	F_{5441}	0.15	F_{6651}	−0.07
F_{331}	0.0109	F_{662}	−0.2523	F_{4332}	−0.23	F_{5442}	0.15	F_{6652}	−0.02
F_{332}	0.2268	F_{663}	−0.0224	F_{4333}	−0.07	F_{5443}	−0.24	F_{6653}	0.02
F_{333}	−57.4227	F_{664}	−0.0940	F_{4411}	−0.59	F_{5444}	−0.18	F_{6654}	−0.02
F_{411}	−0.6925	F_{665}	−0.0227	F_{4421}	3.70	F_{5511}	−0.65	F_{6655}	−0.25
F_{421}	−1.2383			F_{4422}	1.37	F_{5521}	0.73	F_{6666}	−0.49
F_{422}	−1.6381			F_{4431}	0.36	F_{5522}	−0.64		

desired ν_4 state. Hence, more basis functions in the computation converged the actual ν_4 state to within 2.5 cm^{-1} of the condensed phase result while the $2\nu_1$ (formerly the VCI-s ν_4) state cannot correlate to the experimental fundamental for ν_4 since it converges to 970.0 cm^{-1}. Unfortunately, the difference in frequencies for ν_6, the torsional mode, between VPT and VCI-l means that the good correlation between the VCI-s and the condensed phase experimental result is no longer valid. However, the inclusion of more basis functions for the other five modes appears to indicate that the VCI-l results are more trustworthy on the whole. Hence, it appears as though the actual gas phase frequency for ν_6 is probably lower than the condensed phase by as much as 20 cm^{-1}.

Other computations involving fewer basis functions indicate that smaller VCI matrices can adequately describe the zero-point, ν_2, ν_3 and ν_5 modes, i.e., their energies do not change by more than 1 cm^{-1} with the inclusion of more functions. However, a reasonable description of ν_4 and ν_6 requires a larger number of VCI basis functions with convergence experienced at around 15000 a′ functions and 10 000 a″ functions in the CI matrices where the crossing for the $2\nu_1$ and ν_4 states mentioned in the previous paragraph is properly managed with this many functions. Interestingly, the ν_1 mode is actually the one that forces the use of the most basis functions. Its convergence to 1 cm^{-1} is not reached until the number of basis functions defined for VCI-l are used. The large numbers of functions necessary to reach convergence is simply a result of the higher energy region in which this fundamental frequency exists. Hence, truly massive computations must be employed to treat adequately all the states in the *trans*-HOCO radical. Subsequently, convergence of the VCI computations is not necessarily proven when the differences between 4MR and 5MR are small but when the size of the normal coordinate basis sets is adequate.

The largest frequency difference in the fundamental modes between VPT and VCI-l is the ν_6 torsional mode, but this type of disagreement between the two approaches for a torsional mode is not uncommon. Even so, the other five modes are at similar levels of agreement between VPT and VCI as those observed in previous work on other systems,[37] and the disagreement for ν_6 between VPT and VCI is not beyond the scope of reasonable results for each of the methods. This discrepancy is most likely the result of a large anharmonicity for this coordinate where QFFs may not be adequate to describe this behavior even with the QFF in a coordinate system that has better limiting behavior. Regardless, the experimental data for the gas phase frequencies of ν_1 and ν_2, 3635.702 cm^{-1} and 1852.567 cm^{-1}, respectively, shown in Table II, are less than 9 cm^{-1} (5 cm^{-1} for the VCI-l ν_1) lower than the CcCRE QFF-based values, with either VPT and VCI-l. This difference is also in line with previous studies.[37] Such agreement gives strength to our case of making predictions for the other four fundamental modes.

It is interesting to note that the VPT frequency for ν_6 is much closer to the condensed phase experimental result than the VCI-l. However, VPT is over 5 cm^{-1} below the frequency of this mode even when compared to the results of the condensed phase experiment, but the relationship of the condensed phase frequency for the fundamental and the gas phase frequency has not been established. VCI-l predicts a ν_6 frequency that is even further below the VPT indicating that the gas phase frequency of this mode behaves differently than the corresponding condensed phase result. The frequencies of the other three modes for which there is no current gas phase experimental data, ν_3, ν_4, and ν_5, are higher in energy for both VPT and VCI-l than the condensed phase results. Furthermore, these predicted frequencies are close enough to the condensed phase results to give strong indication that the predicted fundamental frequencies of ν_3, ν_4, and ν_5 are reliable and potentially quite close to the actual gas phase values. Although the ν_6 frequency gives pause, the other five modes and even ν_6, as well, give no indication of being markedly erroneous with either method, and these results should help to give more than a qualitative picture to what the fundamental gas phase vibrational frequencies of *trans*-HOCO actually are.

As a final consideration, the exclusion of terms from Eq. (1) in the CcCRE QFF results in some rather fascinating changes in the computed fundamental vibrational frequencies. The averaged coupled-pair functional (ACPF) method has been previously utilized to compute the higher-order electron correlation terms,[33–35] but it was found to lead to the prediction of fundamental vibrational frequencies that were too low in energy. This phenomenon led to our present use of CCSDT as a means to describe this component of the energy at each point. However, the experimental agreement for the CcCRE QFF ν_1 and ν_2 was not as close as desired. Excluding the higher-order electron correlation term in the CcCRE QFF results in the CcCR QFF. Removal of this correction does not greatly change the equilibrium geometry; the bond lengths remain the same up to 0.001 Å while the O_1-C-O_2 bond angle is slightly increased to 127.081° and the $H-O_1-C$ bond angle is decreased by only about 0.1° to 107.895°. The ν_1 fundamental computed with the CcCR QFF is actually 3.5 cm^{-1} closer to the experimental gas phase result than the full CcCRE QFF (all shown in Table II), but the CcCR ν_2 frequency is higher by about a third as much for this fundamental. Hence, there is no systematic corrective behavior for the CcCR QFF as compared to the CcCRE QFF, but, nonetheless, these corrections are very small. Such small differences in the equilibrium geometries and the fundamental vibrational frequencies between the CcCR to CcCRE QFFs indicate that the higher-order electron correlation description from CCSDT does not go far enough to describe the full electron correlation, the converse of the issue experienced with the ACPF method.

Additional removal of the core-correlation term (giving rise to the CR QFF) increases each of the *trans*-HOCO equilibrium bond lengths relative to both the CcCRE and CcCR QFFs (1.177 20 Å for $C=O_2$, 1.342 13 Å for $C-O_1$, and 0.962 28 Å for $H-O_1$) while the bond angles are reduced slightly as compared to both of the more descriptive QFFs (126.948° for O_1-C-O_2 and 107.821° for $H-O_1-C$). The CR QFF predicts frequencies within 4 cm^{-1} of the known gas phase fundamentals for VPT and VCI-l for both ν_1 and ν_2 even though ν_1 is predicted to be lower than experiment with VCI-l while ν_2 is higher than experiment. Besides these two modes, two of other four CR vibrational frequencies are

also lower in energy than their CcCRE counterparts with ν_3 coming in slightly higher for the CR QFF. However, ν_6 is noticeably higher for the CR QFF than the CcCRE. This does bring ν_6 closer to the condensed phase experimental results by about 3.5 cm^{-1} as compared to the CcCRE results and an even larger 6.5 cm^{-1} closer than the CcCR QFF.

This seemingly better result is merely an artifact of error cancellation in this less descriptive QFF and is not a robust reflection of its ability to predict accurately the fundamental vibrational frequencies for which there is no experimental data. The use of only relativistic corrections to a CBS energy in the computation of a QFF mainly influences those modes where bond distance plays an important role, as is seen in the changes to the geometrical parameters listed above. Hence, the same issue with the VPT prediction of ν_6 is present in these two QFFs as it is in the CcCRE results, but it is interesting to note that the CcCRE QFF has better agreement between VPT and VCI-l than the CcCR QFF showcasing the need for higher-order electron-correlation effects to be considered at some level. Even though the CcCR and CR QFFs appear to predict better fundamental frequencies than the CcCRE QFF, these results are not robustly or conceptually better but can serve to help inform the energy range in which the actual fundamentals may be found, especially since the frequencies of the four experimentally unknown modes differ between the three QFFs by less than 6 cm^{-1} and more often by less than 4 cm^{-1}. Additionally, the inclusion of better higher-order electron correlation methods should probably overcome the deficiencies of both the current CcCRE QFF and those utilized previously containing the ACPF method.

IV. CONCLUSIONS

We have carried out an anharmonic vibrational analysis and computed various spectroscopic constants for the $X\ ^2A'$ *trans*-HOCO radical using a highly accurate quartic force field composed of aTZ, aQZ, and a5Z complete basis set extrapolated energies corrected for core correlation, scalar relativistic, and higher-order electron correlation effects, the CcCRE QFF. The composite energy makes exclusive use of coupled cluster theory, established as one of the most accurate chemical theories to date,[70,71] and includes terms necessary to account for most of the deficiencies present in regular quantum chemical models. This QFF was hoped to be the most reliable computed thus far, but the failings of the CCSDT higher-order electron correlation effects hindered its performance. The CR QFF appears to treat this system more accurately, but this is probably the result of fortunate error cancellation.

Our gas phase CcCRE results corroborate the known experimental gas phase frequencies to within 5 cm^{-1} for the O−H stretch (ν_1) and 9 cm^{-1} for the C=O stretch (ν_2) while the CR QFF predicts these values to within 3 cm^{-1} and 3.5 cm^{-1}, respectively. Additionally, both VPT and VCI-l predict some vibrational frequencies to be below even the condensed phase experimental data: the torsional mode (ν_6) for each QFF, the CR ν_4 mode (C−O stretch), and the CR VPT ν_5 mode (O_1-C-O_2 bend). With this calibration and knowledge of behavior, we can conclude that our VCI-l and VPT CcCRE QFF-based fundamental frequencies should be within 9 cm^{-1} or less of their actual gas phase values and the CR QFF-based fundamental frequencies should be within 4 cm^{-1} or less. Hence, removal of the higher-order electron correlation terms from the CcCRE QFF in the CcCR and CR QFFs and removal of the core-correlation terms in the CR QFF coupled with the resulting cancellation of errors leads to better agreement with experiment. The CCSDT correction to CCSD(T) utilized here is not descriptive enough for higher-order electron correlation as it adds only 0.1% of the stabilization energy as compared to the core-correlation, and better terms for this correction should be incorporated in future studies. Furthermore, in order to describe adequately this system using the variational VCI method, large numbers of vibrational variational basis functions must be used, especially for the ν_6, ν_4, and even the ν_1 (O−H stretch) modes where the ν_1 mode shows the most marked improvement for the use of more basis functions. Finally, the relatively large difference in the frequency of the ν_6 mode between VPT and VCI-l regardless of the choice of QFF indicates that the sizable anharmonicity for this mode may not be adequately described using only a QFF.

In short, our results indicate that the CcCRE, CcCR, and CR QFF VCI-l fundamental frequencies (utilizing a large enough number of basis functions) are trustworthy enough to help elucidate what the four unknown gas phase fundamental vibrational frequencies of *trans*-HOCO are. Additionally, we are providing a highly accurate set of other spectroscopic constants for the *trans*-HOCO radical in the gas phase. Those constants previously experimentally determined match our computations to 1% deviation or better, and the rest should likely be similarly accurate for comparison either to laboratory, atmospheric, or planetary observation.

ACKNOWLEDGMENTS

The work done by T.D.C. and R.C.F. is supported by the U.S. National Science Foundation (NSF) award CHE-1058420 and by a Multi-User Chemistry Research Instrumentation and Facility (CRIF:MU) award CHE-0741927. R.C.F. also wishes to thank the Virginia Space Grant Consortium for a Graduate Research Fellowship which he has been grateful to receive for the past three years and T.J.L. and X.H. for their guidance and patience with him throughout this research process and during his visit in the spring of 2011. T.J.L. acknowledges funding from the NASA Herschel GO Program, Cycle 0 TR/LA PID 1022, and NASA (Grant No. 08-APRA08-0050). X.H. is funded by NASA/SETI Institute Cooperative Agreement NNX09AI49A. T.D.C. and R.C.F. wish to thank Dr. Andrew Simmonett of the University of Georgia for the use of his CheMVP program used to generate Fig. 1.

[1] D. E. Milligan and M. E. Jacox, J. Chem. Phys. **54**, 927 (1971).
[2] I. W. M. Smith and R. Zellner, J. Chem. Soc., Faraday Trans. **69**, 1617 (1973).
[3] J. Barker and D. Golden, Chem. Rev. **103**, 4577 (2003).
[4] R. A. Marcus, *Applications of Theoretical Methods to Atmospheric Sciences*, Advances in Quantum Chemistry Vol. 55 (Elsevier, Amsterdam, 2008), pp. 5–19.

[5]J. S. Francisco, J. T. Muckerman, and H.-G. Yu, Acc. Chem. Res. **43**, 1519 (2010).
[6]G. A. Soffen, Science **194**, 1274 (1976).
[7]S. K. Atreya and Z. G. Gu, J. Geophys. Res., [Planets] **99**, 13133, doi:10.1029/94JE01085 (1994).
[8]K. Zahnle, R. M. Haberle, D. C. Catling, and J. F. Kasting, J. Geophys. Res., [Planets] **113**, E11004, doi:10.1029/2008JE003160 (2008).
[9]M. Huang and S. Fabris, J. Phys. Chem. C **112**, 8643 (2008).
[10]V. Formisano, S. Atreya, T. Encrenaz, N. Ignatiev, and M. Giuranna, Science **306**, 1758 (2004).
[11]J. T. Petty and C. B. Moore, J. Mol. Spectrosc. **161**, 149 (1993).
[12]T. J. Sears, W. M. Fawzy, and P. M. Johnson, J. Chem. Phys. **97**, 3996 (1992).
[13]M. E. Jacox, J. Chem. Phys. **88**, 4598 (1988).
[14]D. Forney, M. E. Jacox, and W. E. Thompson, J. Chem. Phys. **119**, 10814 (2003).
[15]M. Mladenovic, J. Chem. Phys. **112**, 1070 (2000).
[16]P. Botschwina and R. Oswald, J. Chem. Phys. **129**, 044305 (2008).
[17]K. Aoki, Chem. Phys. Lett. **323**, 55 (2000).
[18]J. Cernicharo, M. Guèlin, M. Agundez, M. C. McCarthy, and P. Thaddeus, Astrophys. J. **688**, L83 (2008).
[19]H. Yu, J. Muckerman, and T. Sears, Chem. Phys. Lett. **349**, 547 (2001).
[20]T. G. Clements, R. E. Continetti, and J. S. Francisco, J. Chem. Phys. **117**, 6478 (2002).
[21]H. Yu and J. Muckerman, J. Chem. Phys. **117**, 11139 (2002).
[22]G. Poggi and J. S. Francisco, J. Chem. Phys. **120**, 5073 (2004).
[23]H. Yu, J. Muckerman, and J. Francisco, J. Phys. Chem. A **109**, 5230 (2005).
[24]H. Yu and J. Muckerman, J. Phys. Chem. A **110**, 5312 (2006).
[25]H.-G. Yu, J. T. Muckerman, and J. S. Francisco, J. Chem. Phys. **127**, 094302 (2007).
[26]H.-G. Yu, J. S. Francisco, and J. T. Muckerman, J. Chem. Phys. **129**, 064301 (2008).
[27]H.-G. Yu and J. S. Francisco, J. Chem. Phys. **128**, 244315 (2008).
[28]H.-G. Yu, G. Poggi, J. S. Francisco, and J. T. Muckerman, J. Chem. Phys. **129**, 214307 (2008).
[29]H.-G. Yu and J. S. Francisco, J. Phys. Chem. A **113**, 3844 (2009).
[30]G. Poggi and J. S. Francisco, J. Chem. Phys. **130**, 124306 (2009).
[31]H.-G. Yu and J. S. Francisco, J. Phys. Chem. A **113**, 12932 (2009).
[32]C. J. Johnson, B. L. J. Poad, B. B. Shen, and R. E. Continetti, J. Chem. Phys. **134**, 171106 (2011).
[33]X. Huang and T. J. Lee, J. Chem. Phys. **129**, 044312 (2008).
[34]X. Huang, D. W. Schwenke, and T. J. Lee, J. Chem. Phys. **129**, 214304 (2008).
[35]X. Huang and T. J. Lee, J. Chem. Phys. **131**, 104301 (2009).
[36]X. Huang, D. W. Schwenke, and T. J. Lee, J. Phys. Chem. A. **113**, 11954 (2009).
[37]X. Huang, P. R. Taylor, and T. J. Lee, J. Phys. Chem. A **115**, 5005 (2011).
[38]R. C. Fortenberry, R. A. King, J. F. Stanton, and T. D. Crawford, J. Chem. Phys. **132**, 144303 (2010).
[39]T. J. Mach, R. A. King, and T. D. Crawford, J. Phys. Chem. A **114**, 8852 (2010).
[40]R. C. Fortenberry and T. D. Crawford, "Electronically excited states of interstellar molecules," Annu. Rep. Comput. Chem. (in press).
[41]R. C. Fortenberry and T. D. Crawford, J. Chem. Phys. **134**, 154304 (2011).
[42]R. C. Fortenberry and T. D. Crawford, J. Phys. Chem. A **115**, 8119 (2011).
[43]T. J. Lee, J. M. L. Martin, and P. R. Taylor, J. Chem. Phys. **102**, 254 (1995).
[44]C. E. Dateo, T. J. Lee, and D. W. Schwenke, J. Chem. Phys. **101**, 5853 (1994).
[45]J. M. L. Martin, T. J. Lee, P. R. Taylor, and J.-P. François, J. Chem. Phys. **103**, 2589 (1995).
[46]J. D. Watts, J. Gauss, and R. J. Bartlett, J. Chem. Phys. **98**, 8718 (1993).
[47]K. Raghavachari, G. W. Trucks, J. A. Pople, and M. Head-Gordon, Chem. Phys. Lett. **157**, 479 (1989).
[48]T. H. Dunning, J. Chem. Phys. **90**, 1007 (1989).
[49]K. A. Peterson and T. H. Dunning, J. Chem. Phys. **102**, 2032 (1995).
[50]J. M. L. Martin and P. R. Taylor, Chem. Phys. Lett. **225**, 473 (1994).
[51]R. A. Kendall, T. H. Dunning, and R. J. Harrison, J. Chem. Phys. **96**, 6796 (1992).
[52]J. M. L. Martin and T. J. Lee, Chem. Phys. Lett. **258**, 136 (1996).
[53]M. Douglas and N. Kroll, Ann. Phys. **82**, 89 (1974).
[54]As discussed in Refs. 33 and 37, the quality of the computation was not seen to increase with the use of larger ζ numbers in the basis set for the inclusion of relativistic corrections. Hence, only the TZ computations are necessary.
[55]J. Noga and R. J. Bartlett, J. Chem. Phys. **86**, 7041 (1987).
[56]J. D. Watts and R. J. Bartlett, J. Chem. Phys. **93**, 6104 (1990).
[57]CFOUR, a quantum chemical program package written by J. F. Stanton, J. Gauss, M. E. Harding, P. G. Szalay with contributions from A. A. Auer, R. J. Bartlett, U. Benedikt, C. Berger, D. E. Bernholdt, Y. J. Bomble, O. Christiansen, M. Heckert, O. Heun, C. Huber, T.-C. Jagau, D. Jonsson, J. Juslius, K. Klein, W. J. Lauderdale, D. A. Matthews, T. Metzroth, D. P. O'Neill, D. R. Price, E. Prochnow, K. Ruud, F. Schiffmann, S. Stopkowicz, A. Tajti, J. Vázquez, F. Wang, J. D. Watts, and the integral packages MOLECULE (J. Almlöf and P. R. Taylor), PROPS (P. R. Taylor), ABACUS (T. Helgaker, H. J. Aa. Jensen, P. Jørgensen, and J. Olsen), and ECP routines by A. V. Mitin and C. van Wüllen. For the current version, see http://www.cfour.de.
[58]H.-J. Werner, P. J. Knowles, F. R. Manby, M. Schütz *et al.*, MOLPRO, version 2010.1, a package of *ab initio* programs, 2010, see http://www.molpro.net.
[59]INTDER 2005 is a general program written by W. D. Allen and co-workers, which performs vibrational analysis and higher-order nonlinear transformations, 2005.
[60]J. F. Gaw, A. Willets, W. H. Green, and N. C. Handy, SPECTRO program, version 3.0, 1996.
[61]I. M. Mills, in *Molecular Spectroscopy – Modern Research*, edited by K. N. Rao and C. W. Mathews (Academic, New York, 1972).
[62]J. K. G. Watson, in *Vibrational Spectra and Structure*, edited by J. R. During (Elsevier, Amsterdam, 1977).
[63]D. Papousek and M. R. Aliev, *Molecular Vibration-Rotation Spectra* (Elsevier, Amsterdam, 1982).
[64]S. Carter, J. M. Bowman, and N. C. Handy, Theor. Chim. Acta **100**, 191 (1998).
[65]J. M. Bowman, S. Carter, and X. Huang, Int. Rev. Phys. Chem. **22**, 533 (2003).
[66]T. Oyama, W. Funato, Y. Sumiyoshi, and Y. Endo, J. Chem. Phys. **134**, 174303 (2011).
[67]P. Botschwina, Mol. Phys. **103**, 1441 (2005).
[68]H. E. Radford, W. Wei, and T. J. Sears, J. Chem. Phys. **97**, 3989 (1992).
[69]D. Feller, D. A. Dixon, and J. S. Francisco, J. Phys. Chem. A **107**, 1604 (2003).
[70]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), pp. 47–108.
[71]T. Helgaker, T. A. Ruden, P. Jørgensen, J. Olsen, and W. Klopper, J. Phys. Org. Chem. **17**, 913 (2004).