

Performance of W4 theory for spectroscopic constants and electrical properties of small molecules

Amir Karton and Jan M. L. Martin

Citation: *The Journal of Chemical Physics* **133**, 144102 (2010); doi: 10.1063/1.3489113

View online: <http://dx.doi.org/10.1063/1.3489113>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/133/14?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

The chemical bond in external electric fields: Energies, geometries, and vibrational Stark shifts of diatomic molecules

J. Chem. Phys. **139**, 144101 (2013); 10.1063/1.4820487

Interaction-induced dipoles of hydrogen molecules colliding with helium atoms: A new ab initio dipole surface for high-temperature applications

J. Chem. Phys. **136**, 044320 (2012); 10.1063/1.3676406

Calculation of the structure, potential energy surface, vibrational dynamics, and electric dipole properties for the Xe:HI van der Waals complex

J. Chem. Phys. **134**, 174302 (2011); 10.1063/1.3583817

Automatic generation of force fields and property surfaces for use in variational vibrational calculations of anharmonic vibrational energies and zero-point vibrational averaged properties

J. Chem. Phys. **125**, 124108 (2006); 10.1063/1.2352734

Relativistic and correlation effects on molecular properties: The interhalogens CIF, BrF, BrCl, IF, ICl, and IBr

J. Chem. Phys. **108**, 5177 (1998); 10.1063/1.476314



NEW Special Topic Sections

NOW ONLINE
Lithium Niobate Properties and Applications:
Reviews of Emerging Trends

AIP | Applied Physics
Reviews

Performance of W4 theory for spectroscopic constants and electrical properties of small molecules

Amir Karton and Jan M. L. Martin^{a)}

Department of Organic Chemistry, Weizmann Institute of Science, IL-76100 Rehovot, Israel

(Received 7 July 2010; accepted 24 August 2010; published online 11 October 2010)

Accurate spectroscopic constants and electrical properties of small molecules are determined by means of W4 and post-W4 theories. For a set of 28 first- and second-row diatomic molecules for which very accurate experimental spectroscopic constants are available, W4 theory affords near-spectroscopic or better predictions. Specifically, the root-mean-square deviations (RMSDs) from experiment are 0.04 pm for the equilibrium bond distances (r_e), 1.03 cm⁻¹ for the harmonic frequencies (ω_e), 0.20 cm⁻¹ for the first anharmonicity constants ($\omega_e x_e$), 0.10 cm⁻¹ for the second anharmonicity constants ($\omega_e y_e$), and 0.001 cm⁻¹ for the vibration-rotation coupling constants (α_e). These RMSDs imply 95% confidence intervals of about 0.1 pm for r_e , 2.0 cm⁻¹ for ω_e , 0.4 cm⁻¹ for $\omega_e x_e$, and 0.2 cm⁻¹ for $\omega_e y_e$. We find that post-CCSD(T) contributions are essential to achieve such narrow confidence intervals for r_e and ω_e , but have little effect on $\omega_e x_e$ and α_e , and virtually none on $\omega_e y_e$. Higher-order connected triples \hat{T}_3 -(T) improve the agreement with experiment for the hydride systems, but their inclusion (in the absence of \hat{T}_4) tends to worsen the agreement with experiment for the nonhydride systems. Connected quadruple excitations \hat{T}_4 have significant and systematic effects on r_e , ω_e , and $\omega_e x_e$, in particular they universally increase r_e (by up to 0.5 pm), universally reduce ω_e (by up to 32 cm⁻¹), and universally increase $\omega_e x_e$ (by up to 1 cm⁻¹). Connected quintuple excitations \hat{T}_5 are spectroscopically significant for ω_e of the nonhydride systems, affecting ω_e by up to 4 cm⁻¹. Diagonal Born–Oppenheimer corrections have systematic and spectroscopically significant effects on r_e and ω_e of the hydride systems, universally increasing r_e by 0.01–0.06 pm and decreasing ω_e by 0.3–2.1 cm⁻¹. Obtaining r_e and ω_e of the pathologically multireference BN and BeO systems with near-spectroscopic accuracy requires large basis sets in the core-valence CCSD(T) step and augmented basis sets in the valence post-CCSD(T) steps in W4 theory. The triatomic molecules H₂O, CO₂, and O₃ are also considered. The equilibrium geometries and harmonic frequencies (with the exception of the asymmetric stretch of O₃) are obtained with near-spectroscopic accuracy at the W4 level. The asymmetric stretch of ozone represents a severe challenge to W4 theory, in particular the connected quadruple contribution converges very slowly with the basis set size. Finally, the importance of post-CCSD(T) correlation effects for electrical properties, namely, dipole moments (μ), polarizabilities (α), and first hyperpolarizabilities (β), is evaluated. © 2010 American Institute of Physics. [doi:10.1063/1.3489113]

I. INTRODUCTION

Since the early 1990s, there has been growing interest in calculating accurate *ab initio* anharmonic force fields for small molecules. There are two aspects to be considered: (i) the nuclear vibrational analysis and (ii) the level of the electronic structure calculations. For diatomic molecules (i) is relatively straightforward using a Dunham analysis, and for rigid triatomic molecules, such as those considered in the present work, (i) entails no serious problems. As for (ii), for systems with mild to moderate nondynamical correlation effects, the accuracy of CCSD(T) basis set limit results is on

the order of 5–10 cm⁻¹ for harmonic frequencies^{1–5} and 0.1–0.5 pm for bond lengths.^{1,2,6,7} To surpass this level of accuracy (or when considering molecules with more pronounced multireference character such as C₂, BN, BeO, and O₃) one should consider multireference methods^{8–10} or post-CCSD(T) contributions.^{4–7,11} Recently, Mintz *et al.*¹² applied the multireference ccCA method¹³ to compute the potential energy curves of N₂ and C₂; they obtained errors of ~0.06 pm for the bond lengths and ~2 cm⁻¹ for the harmonic frequencies.

The determination of very precise molecular energies (atomization energies or enthalpies of formation) has been one of the primary goals of composite *ab initio* methods. It has been shown that highly accurate thermochemical protocols such as HEAT^{14–16} and W4^{17,18} are capable of sub-kJ/

^{a)}Present address: Department of Chemistry, University of North Texas, Denton, TX 76203-5017. Electronic addresses: gershom@unt.edu and gershom@weizmann.ac.il.

mol accuracy on average (see Ref. 19 for a recent review). In particular, W4 theory obtains a root-mean-square deviation (RMSD) of 0.08 kcal/mol against a test set of 25 first- and second-row small molecules for which very accurate ATcT (Ref. 20) atomization energies are available. This implies a 95% confidence interval of ~ 0.16 kcal/mol; the mean signed deviation (MSD) of just -0.01 kcal/mol suggests that W4 is free of systematic bias. Worst-case errors for problematic molecules are < 1 kJ/mol: for example, for F_2O_2 ,²¹ C_2 ,¹⁸ F_2O ,²¹ and O_3 ,¹⁷ W4 is 0.09, 0.17, 0.18, and 0.23 kcal/mol away from the ATcT atomization energies (the ATcT value for C_2 is available in Ref. 22 and for the remaining species in Ref. 23). In our continued work in this field we have shown that contributions from successively higher cluster expansion terms converge increasingly faster with the basis set, as they increasingly reflect nondynamical rather than dynamical correlation.^{17,18} Indeed, the fact that W4 theory and related methods can be carried out at all at a realistic cost hinges on this behavior.

In view of the success of W4 theory for thermochemical properties^{17,18,21} it is of interest to establish the reliability of W4 (and related) methods for spectroscopic properties based on energy derivatives with respect to the nuclear coordinates (e.g., r_e , ω_e , and $\omega_e x_e$) and for electrical properties based on energy derivatives with respect to an external static electric field (e.g., μ , α , and β).

The present study considers a chemically diverse data set of 31 first- and second-row diatomic molecules as well as the triatomic molecules H_2O , CO_2 , and O_3 . The chosen set, which includes radicals, polar systems, hydrides, and nonhydrides with single and multiple bonds, evidently spans a wide gamut from systems dominated by dynamical correlation (e.g., BH and H_2O) to systems with pathological nondynamical correlation (e.g., C_2 , BN, BeO, and O_3) and all shades in between.

II. COMPUTATIONAL METHODS

A. Electronic structure

All the SCF, CCSD, and CCSD(T) calculations were carried out using MOLPRO 2009.1 (Ref. 24) running on the Martin group Linux cluster at the Weizmann Institute. The post-CCSD(T) calculations were carried out using MRCC interfaced to the MOLPRO program suite.²⁵ The diagonal Born–Oppenheimer correction (DBOC) calculations were carried out using the CFOUR program system.²⁶ All basis sets employed belong to the correlation consistent family of Dunning and co-workers.^{27–31} The notation aug'-cc-pV($n+d$)Z indicates the combination of regular cc-pV n Z on hydrogen and aug-cc-pV($n+d$)Z on other elements.

The computational protocols of W4, W4.2, and W4.3 theories have been specified and rationalized in great detail elsewhere.^{17,18} In the present work the steps involved in W4 theory are divided in the following manner:

- W4 [up to CCSD(T)_{fc,nr}] represents the clamped-nuclei, nonrelativistic CCSD(T) infinite basis set limit energy in the frozen-core approximation (in which the $1s$ orbitals for first-row atoms and the $1s$, $2s$, and $2p$ orbitals for

second-row atoms are constrained to be doubly occupied in all configurations). The fc and nr subscripts stand for “frozen-core” and “nonrelativistic.” The following extrapolations are used for the HF, CCSD, and (T) contributions:

- The ROHF-SCF contribution is extrapolated from the aug'-cc-pV(5+d)Z and aug'-cc-pV(6+d)Z basis sets using the Karton–Martin modification³² of Jensen's extrapolation formula.³³
 - The RCCSD valence correlation energy is calculated from these same basis sets. Following the suggestion of Klopper,³⁴ it is partitioned into singlet-coupled pair energies, triplet-coupled pair energies, and \hat{T}_1 terms. The singlet-coupled and triplet-coupled pair energies are extrapolated using the $A+B/L^\alpha$ two-point extrapolation formula (where L is the highest angular momentum present in the basis set) with $\alpha_S=3$ and $\alpha_T=5$, respectively, and the \hat{T}_1 term (which exhibits very weak basis set dependence) is set equal to that in the largest basis set.
 - The (T) valence correlation energy is extrapolated from the aug'-cc-pV(Q+d)Z and aug'-cc-pV(5+d)Z basis sets using the $A+B/L^3$ two-point extrapolation formula. For open-shell systems the Werner–Knowles–Hampel³⁵ (also known as MOLPRO) definition of the restricted open-shell CCSD(T) energy is employed throughout, rather than the original Watts–Gauss–Bartlett³⁶ (also known as ACES II/CFOUR) definition.
- W4 [up to CCSD(T)] in addition includes inner-shell correlation and scalar relativistic contributions. The former is extrapolated from RCCSD(T)/aug'-cc-pwCVTZ and RCCSD(T)/aug'-cc-pwCVQZ energies using the $A+B/L^3$ two-point extrapolation formula, and the latter (in the second-order Douglas–Kroll–Hess approximation^{37,38}) is obtained from the difference between nonrelativistic CCSD(T)/aug'-pV(Q+d)Z and relativistic CCSD(T)/aug'-cc-pV(Q+d)Z-DK calculations.³¹
 - W4 [up to CCSDT] additionally includes higher-order connected triples \hat{T}_3 –(T) valence correlation contribution extrapolated from the cc-pVDZ and cc-pVTZ basis sets using the $A+B/L^3$ two-point extrapolation formula.
 - In W4 [up to CCSDTQ] the connected quadruples \hat{T}_4 term is also included. The valence correlation (Q) and \hat{T}_4 –(Q) contributions are calculated with the cc-pVTZ and cc-pVDZ basis sets, respectively. In Refs. 17 and 18 we found that scaling their sum by 1.10 offers a very reliable (as well as fairly cost-effective) estimate of the basis set limit \hat{T}_4 contribution.
 - Adding the connected quintuple \hat{T}_5 valence correlation contribution calculated with the sp part of the cc-pVDZ basis set—denoted cc-pVDZ (no d)—results in full W4

TABLE I. Equilibrium bond distances (r_e , picometer) of diatomic molecules obtained from a Dunham analysis of potential energy curves computed at the W4 and related levels.

	W4 [up to CCSD(T) _{fc,nr}]	W4 [up to CCSD(T)]	W4 [up to CCSDT]	W4 [up to CCSDTQ]	W4	W4.2	W4.3	Δ DBOC ^a	Expt.	Ref.
BH	123.25	122.90	122.91	122.91	122.91	122.91	122.92	0.060	122.95	60
CH	111.96	111.75	111.77	111.77	111.78			0.041	111.777	2
NH	103.68	103.55	103.58	103.60	103.60			0.026	103.655	2
OH	97.01	96.92	96.93	96.96	96.96			0.015	96.966	61
HF	91.73	91.67	91.66	91.69	91.69	91.69	91.69	0.005	91.6984	2
AlH	164.99	164.48	164.53	164.54	164.54			0.053	164.5362	62
SiH	152.18	151.81	151.85	151.86	151.86			0.039	151.966	63
PH	142.35	142.06	142.11	142.13	142.13			0.028	142.14	64
SH	134.21	133.96	133.99	134.01	134.01			0.020	134.0614	65
HCl	127.62	127.41	127.42	127.44	127.44	127.44	127.45	0.013	127.461 49	66
N ₂	109.89	109.65	109.58	109.73	109.75	109.75	109.75	0.001	109.768 ₅	61
O ₂	120.61	120.42	120.33	120.66	120.70			0.000	120.752	61
F ₂	140.93	140.81	140.75	141.17	141.18	141.20	141.23	0.000	141.193	61
Si ₂	225.09	224.08	224.22	224.52	224.54			0.002	224.6	61
P ₂	189.76	188.95	188.77	189.23	189.27	189.30		0.001	189.34	61
S ₂	189.14	188.57	188.55	188.85	188.87			0.001	188.92	61
Cl ₂	198.87	198.47	198.55	198.70	198.70	198.71		0.001	198.7 ₉	61
BF	126.66	126.21	126.21	126.24	126.23			0.001	126.25 ₉	61
CO	113.02	112.75	112.72	112.80	112.80	112.80	112.81	0.001	112.824 27	66
BCl	172.19	171.41	171.45	171.49	171.48			0.000	171.5283	67
CS	153.86	153.31	153.30	153.45	153.45	153.45		0.001	153.4941	61
SiO	151.42	150.82	150.78	150.95	150.93			0.001	150.9739	61
PN	149.35	148.81	148.63	149.00	149.05			0.001	149.0866	61
SO	148.23	147.87	147.77	148.05	148.08			0.000	148.1087	61
AlF	166.19	165.40	165.40	165.42	165.42			0.001	165.4369	61
ClF	162.74	162.52	162.55	162.75	162.76			0.001	162.8313	61
AlCl	213.87	212.91	212.94	212.96	212.96			0.001	213.0113	61
SiS	193.49	192.67	192.68	192.88	192.85			0.001	192.9264	68
Error statistics for hydrides (10 systems) ^b										
MSD	0.21	-0.04	-0.01	0.00	0.00					
MAD	0.21	0.04	0.03	0.03	0.03					
RMSD	0.25	0.06	0.04	0.03	0.03					
Error statistics for nonhydrides (18 systems) ^b										
MSD	0.30	-0.23	-0.26	-0.05	-0.04					
MAD	0.36	0.23	0.26	0.05	0.04					
RMSD	0.43	0.27	0.30	0.06	0.05					
Error statistics for everything (28 systems) ^b										
MSD	0.27	-0.16	-0.17	-0.04	-0.03					
MAD	0.30	0.17	0.18	0.05	0.04					
RMSD	0.33	0.22	0.25	0.05	0.04					

^aDBOC correction at the HF/AVTZ level.^bMean signed deviations (MSDs), mean absolute deviation (MAD), and root-mean-square deviation (RMSD) from experiment. Note that the DBOC corrections (cf. footnote a) are included in the error statistics.

theory. The \hat{T}_3 contribution converges very rapidly with the basis set as it primarily represents static correlation.^{17,18}

W4 represents an approximation to the relativistic basis-set limit CCSDTQ5 energy. The DBOC contributions, calculated at the ROHF/aug'-cc-pVTZ level of theory, are reported separately in Tables I–V, and are included in the final error statistics presented in these tables.

For the smaller systems we also consider the post-W4

methods (W4.2 and W4.3) as defined in Ref. 17. The changes in W4.2 and W4.3 relative to W4 are summarized as follows:

- W4.2 theory in addition takes account of the \hat{T}_3 -(T) correction to the core-valence contribution obtained using the cc-pwCVTZ basis set.
- In W4.3 all the valence post-CCSD(T) corrections are additionally upgraded: the \hat{T}_3 -(T) and (Q) corrections are extrapolated from the cc-pVTZ and cc-pVQZ basis

TABLE II. Harmonic frequencies (ω_e , cm^{-1}) of diatomic molecules obtained from a Dunham analysis of potential energy curves computed at the W4 and related levels.

	W4 [up to CCSD(T) _{fc,nr}]	W4 [up to CCSD(T)]	W4 [up to CCSDT]	W4 [up to CCSDTQ]	W4	W4.2	W4.3	ΔDBOC^a	Expt. ^b
BH	2360.24	2370.79	2369.13	2369.08	2369.08	2369.10	2368.69	-2.08	2366.7296
CH	2858.08	2865.99	2863.57	2862.53	2862.51			-1.83	2860.7508
NH	3286.50	3292.03	3287.33	3284.65	3284.62			-1.43	3282.7200
OH	3742.91	3746.58	3744.10	3739.55	3739.48			-0.90	3737.7610
HF	4141.64	4143.57	4143.71	4138.87	4138.77	4138.79	4138.51	-0.31	4138.3850
AlH	1688.45	1685.17	1682.54	1682.14	1682.14			-1.10	1682.3747
SiH	2048.29	2047.07	2043.63	2042.91	2042.90			-1.04	2042.5229
PH	2370.75	2370.79	2365.80	2364.41	2364.41			-0.91	2363.7740
SH	2700.78	2701.91	2698.64	2696.42	2696.40			-0.73	2696.2475
HCl	2994.17	2995.65	2994.23	2991.50	2991.48	2991.60	2990.94	-0.53	2990.9248
N ₂	2362.34	2371.91	2382.27	2361.83	2358.54	2357.89	2358.21	0.04	2358.5700
O ₂	1605.48	1609.22	1617.24	1585.76	1581.78			0.08	1580.1610
F ₂	931.17	932.34	936.12	919.44	918.96	917.82	917.44	0.02	916.9290
Si ₂	516.41	517.67	516.23	511.23	510.78			0.00	510.9800
P ₂	787.79	792.23	797.62	784.26	782.87	782.10		0.00	780.7700
S ₂	734.42	735.99	736.93	728.16	727.48			0.00	725.7102
Cl ₂	564.79	565.65	564.48	561.28	561.24	560.94		0.00	559.7510
BF	1394.96	1405.01	1404.45	1403.02	1403.25			0.04	1402.1587
CO	2166.60	2176.25	2178.86	2170.22	2170.37	2170.16	2170.35	0.05	2169.7559
BCl	836.91	843.27	841.90	840.74	840.93			0.03	840.2947
CS	1285.98	1292.50	1293.26	1284.95	1285.24	1285.45		0.02	1285.1546
SiO	1241.66	1248.53	1250.98	1241.56	1242.79			0.01	1241.5439
PN	1344.72	1352.54	1363.39	1341.62	1338.13			0.02	1336.9480
SO	1160.68	1163.56	1168.78	1152.64	1151.10			0.00	1150.7913
AlF	799.79	803.09	802.84	802.36	802.44			0.00	802.3245
ClF	791.38	792.11	791.38	784.96	784.81			0.00	783.4534
AlCl	481.75	482.80	482.42	482.11	482.12			0.00	481.7747
SiS	752.61	755.69	755.59	750.30	751.09			0.00	749.6456
Error statistics for hydrides (10 systems) ^c									
MSD	1.88	4.66	1.96	-0.10	-0.13				
MAD	4.49	4.66	2.15	0.48	0.46				
RMSD	4.81	5.09	2.80	0.61	0.60				
Error statistics for nonhydrides (18 systems) ^c									
MSD	4.61	9.11	11.57	1.67	0.97				
MAD	6.41	9.11	11.57	1.69	1.00				
RMSD	8.67	11.22	15.17	2.35	1.21				
Error statistics for everything (28 systems) ^c									
MSD	3.64	7.52	8.14	1.04	0.58				
MAD	5.73	7.52	8.21	1.26	0.80				
RMSD	7.79	9.78	12.69	1.99	1.03				

^aDBOC correction at the HF/AVTZ level.^bFrom Ref. 69.^cSee footnote b of Table I.

sets, the \hat{T}_4 -(Q) and T_5 corrections are calculated with the cc-pVTZ and cc-pVDZ basis sets, respectively, and the \hat{T}_6 correction is calculated with the cc-pVDZ (no d) basis set.

Finally, for the pathologically multireference systems in Table VI (C_2 , BN, and BeO) we also consider two additional extensions of W4 theory:

- Replacing the regular correlation-consistent basis sets on electronegative atoms (N and O) with their aug-

mented versions in all the valence post-CCSD(T) steps in W4 theory.

- Extrapolating the CCSD(T) inner-shell correlation contribution from larger basis sets, namely, the aug-cc-pwCVQZ and aug-cc-pwCV5Z basis sets.

B. Vibrational analysis

For each of the diatomic molecules, a 21-point potential energy curve was calculated using the above-mentioned W4

TABLE III. First-order anharmonic corrections ($\omega_e x_e$, cm^{-1}) of diatomic molecules obtained from a Dunham analysis of potential energy curves computed at the W4 and related levels.

	W4 [up to CCSD(T) _{fc,nr}]	W4 [up to CCSD(T)]	W4 [up to CCSDT]	W4 [up to CCSDTQ]	W4	W4.2	W4.3	ΔDBOC^a	Expt. ^b
BH	48.92	49.16	49.33	49.33	49.33	49.34	49.33	-0.02	49.339 83
CH	63.66	63.89	64.19	64.26	64.26			-0.01	64.4387
NH	77.93	78.07	78.53	78.74	78.74			0.01	79.04
OH	84.38	84.48	84.72	85.01	85.02			0.00	84.8813
HF	89.73	89.83	89.87	90.09	90.10	90.10	90.13	0.01	89.9432
AlH	28.75	28.45	28.59	28.61	28.61			-0.01	29.050 98
SiH	35.67	35.59	35.84	35.89	35.89			-0.01	36.0552
PH	43.10	43.09	43.46	43.58	43.58			0.00	43.907
SH	47.98	48.01	48.25	48.40	48.40			0.00	48.742
HCl	51.89	51.92	52.02	52.18	52.18	52.18	52.16	0.00	52.8
N ₂	13.86	13.90	13.64	14.14	14.24	14.26	14.24	0.00	14.324
O ₂	11.03	11.07	10.85	11.81	11.96			0.00	11.951 27
F ₂	11.45	11.41	11.07	11.40	11.40	11.45	11.44	0.00	11.3221
Si ₂	1.93	1.94	1.92	2.02	2.03			0.00	2.02
P ₂	2.72	2.71	2.68	2.83	2.84	2.86		0.00	2.835
S ₂	2.73	2.73	2.70	2.85	2.86			0.00	2.8582
Cl ₂	2.61	2.59	2.62	2.67	2.67	2.68		0.00	2.694 27
BF	11.71	11.81	11.85	11.86	11.86			0.00	11.821 06
CO	13.11	13.17	13.12	13.33	13.30	13.30	13.27	0.00	13.288 03
BCl	5.37	5.42	5.44	5.47	5.47			0.00	5.4917
CS	6.32	6.37	6.36	6.54	6.52	6.51		0.00	6.502 605
SiO	5.84	5.90	5.83	6.02	5.99			0.00	5.974 37
PN	6.56	6.57	6.44	6.76	6.81			0.00	6.8958
SO	6.16	6.17	6.09	6.47	6.51			0.00	6.4096
AlF	4.78	4.86	4.86	4.86	4.86			0.00	4.849 915
ClF	4.86	4.85	4.84	4.95	4.95			0.00	4.9487
AlCl	2.08	2.10	2.10	2.11	2.11			0.00	2.101 811
SiS	2.52	2.53	2.52	2.61	2.59			0.00	2.586 23
Error statistics for hydrides (10 systems) ^c									
MSD	-0.62	-0.57	-0.34	-0.21	-0.21				
MAD	0.62	0.57	0.34	0.27	0.27				
RMSD	0.68	0.64	0.41	0.32	0.32				
Error statistics for nonhydrides (18 systems) ^c									
MSD	-0.18	-0.15	-0.22	-0.01	0.01				
MAD	0.19	0.17	0.22	0.05	0.03				
RMSD	0.28	0.26	0.35	0.07	0.04				
Error statistics for everything (28 systems) ^c									
MSD	-0.34	-0.30	-0.26	-0.08	-0.07				
MAD	0.35	0.31	0.27	0.13	0.12				
RMSD	0.48	0.45	0.39	0.21	0.20				

^aDBOC correction at the HF/AVTZ level.^bFrom Ref. 69.^cSee footnote b of Table I.

(and related) theories. The single point energy calculations are carried out at bond distances $r_x = r_e^{\text{expt}} + x$ ($x = 0, \pm 1, \pm 2, \dots, \pm 10$ pm), where r_e^{expt} is the experimental equilibrium bond length. The spectroscopic constants (r_e , ω_e , $\omega_e x_e$, $\omega_e y_e$, and α_e) are obtained from a sixth to eighth degree Dunham fit of the potential energy curves.³⁹

For the triatomics CO₂, H₂O, and O₃ grids of all points required to generate the nonvanishing quadratic, cubic, and quartic force constants in symmetry-adapted internal coordinates are calculated using the above-mentioned W4 (and related) theories.

The convergence criteria throughout are tightened such that the SCF and coupled-cluster energies are converged to at least 10^{-12} a.u.

C. Response properties

The dipole moments (μ), static polarizabilities (α), and static hyperpolarizabilities (β) are calculated at the experimental structures via numerical differentiation of energies with respect to a uniform electric field. A field strength of $h=0.0025$ a.u. was chosen as the basic grid size: the values

TABLE IV. Second-order anharmonic corrections ($\omega_e y_e$, cm^{-1}) of diatomic molecules obtained from a Dunham analysis of potential energy curves computed at the W4 and related levels.

	W4 [up to CCSD(T) _{fc,mr}]	W4 [up to CCSD(T)]	W4 [up to CCSDT]	W4 [up to CCSDTQ]	W4	W4.2	W4.3	ΔDBOC^a	Expt. ^b
BH	0.384	0.369	0.359	0.360	0.360	0.359	0.367	0.000	0.362
CH	0.322	0.314	0.301	0.298	0.300			-0.002	0.3634
NH	0.290	0.138	0.113	0.096	0.096			0.001	0.367
OH	0.654	0.518	0.515	0.507	0.507			0.003	0.5409
HF	1.064	1.052	1.063	1.056	1.056	1.056	1.052	0.002	0.924 49
AlH	0.238	-0.030	-0.031	-0.032	-0.032			-0.001	0.247 62
SiH	0.149	0.104	0.095	0.092	0.092			-0.002	0.1254
PH	0.029	0.012	-0.007	-0.015	-0.014			0.001	0.1059
SH	0.065	0.061	0.050	0.040	0.040			0.000	0.1124
HCl	0.021	-0.018	-0.020	-0.027	-0.027	-0.028	-0.028	0.001	0.218 03
Error statistics for hydrides (10 systems) ^c									
MSD	-0.015	-0.084	-0.093	-0.099	-0.099				
MAD	0.075	0.112	0.121	0.126	0.125				
RMSD	0.094	0.147	0.155	0.160	0.160				
Error statistics for everything (28 systems) ^c									
MSD	-0.005	-0.032	-0.034	-0.038	-0.038				
MAD	0.030	0.045	0.049	0.051	0.051				
RMSD	0.061	0.095	0.100	0.103	0.103				

^aDBOC correction at the HF/AVTZ level.^bFrom Ref. 69.^cSee footnote b of Table I.

reported were obtained by means of Richardson extrapolation⁴⁰ from successive multiples of that grid size. The first-order (μ_z) and third-order (β_{zzz}) partial derivatives are obtained by means of a four point formula using static field strengths of $\pm h$ and $\pm 2h$. The second-order derivatives (α_{xx} , α_{yy} , and α_{zz}) are obtained through a five point formula using field strengths of 0, $\pm h$, and $\pm 2h$. The mixed third-order derivatives (β_{jxz} , $j=x,y$) are computed using a six point formula with field strengths of $\pm 2h\hat{z}$, $\pm 2h(\hat{z}+\hat{j})$, and $\pm 2h(\hat{z}-\hat{j})$.

III. RESULTS AND DISCUSSION

A. Multireference considerations

In Ref. 17 we proposed a number of energy-based diagnostics for the importance of nondynamical correlation that are specifically designed for thermochemical purposes. In particular, the %TAE_e[(T)] diagnostic, i.e., the percentage of the total atomization energy accounted for by parenthetical connected triple excitations, proved to be a very efficient and cost-effective *a priori* diagnostic,

$$\%TAE_e[(T)] = 100 \times \frac{TAE_e[\text{CCSD}(T)] - TAE_e[\text{CCSD}]}{TAE_e[\text{CCSD}(T)]}, \quad (1)$$

where $TAE_e[\text{CCSD}]$ and $TAE_e[\text{CCSD}(T)]$ represent, respectively, the nonrelativistic, clamped-nuclei CCSD and CCSD(T) total atomization energies at the bottom of the well. Values of %TAE_e[(T)] are interpreted as follows:¹⁷ below 2% indicates systems dominated by dynamical correlation; 2%–5% mild nondynamical correlation; 5%–10% mod-

erate nondynamical correlation; and in excess of 10% severe nondynamical correlation.

Table S-I of the supporting information⁴⁶ provides the percentage of the nonrelativistic, clamped-nuclei total atomization energy at the bottom of the well accounted for by SCF, (T) triples, post-CCSD(T), and $\hat{T}_4 + \hat{T}_5$ contributions. Table S-I also lists the coupled cluster \mathcal{T}_1 diagnostic,⁴¹ \mathcal{D}_1 diagnostic,⁴² and the largest CCSD T_2 amplitudes. However, the use of these diagnostics as a measure of multireference effects has been criticized by us^{17,21} and by others.^{43–45} In the context of the present work, for example, a \mathcal{T}_1 diagnostic of 0.03 is obtained for CS and SiO as well as for O₃, although the latter is a notoriously multireference system. The \mathcal{D}_1 diagnostic of O₂ (0.01) is the same as, or even smaller than, that of the hydride systems, despite the former having %TAE_e[($\hat{T}_4 + \hat{T}_5$)] values that are almost an order of magnitude greater. The largest T_2 cluster amplitudes are deceptively high for BH (0.11) and deceptively low for BeO (0.04). In practice, the %TAE_e[(T)] indicator proves to be a very useful predictor for the importance of post-CCSD(T) correlation effects (see relevant discussions in Refs. 17 and 21).

As expected, the hydride systems considered in the present study exhibit very mild nondynamical correlation effects and can be regarded as dominated by dynamical correlation: 60%–80% of the atomization energy is accounted for at the SCF level, and only 0%–2% by the (T) triples. The nonhydrides BF, BCl, AlF, AlCl, CO, SiO, SiS, and N₂ are characterized by mild nondynamical correlation: at least 50% of the TAE_e is accounted for at the SCF level, and $2 \leq \%TAE_e[(T)] \leq 5$. The homonuclear diatomics (O₂, Si₂, P₂, S₂, and Cl₂), as well as CS, PN, SO, ClF, and BeO, are

TABLE V. Vibration-rotation coupling constants (α_e , cm^{-1}) of diatomic molecules obtained from a Dunham analysis of potential energy curves computed at the W4 and related levels.

	W4 [up to CCSD(T) _{fc,nr}]	W4 [up to CCSD(T)]	W4 [up to CCSDT]	W4 [up to CCSDTQ]	W4	W4.2	W4.3	ΔDBOC^a	Expt. ^b
BH	0.418 52	0.421 06	0.422 07	0.422 05	0.422 05	0.422 07	0.422 16	-0.000 27	0.421 565
CH	0.531 15	0.533 45	0.535 03	0.535 43	0.535 44			-0.000 26	0.53654
NH	0.643 01	0.645 13	0.647 54	0.648 69	0.648 71			-0.000 18	0.650 38
OH	0.715 15	0.716 97	0.718 30	0.720 05	0.720 09			-0.000 16	0.7242
HF	0.786 93	0.788 54	0.788 93	0.790 43	0.790 47	0.790 48	0.790 48	-0.000 02	0.793 370 4
AlH	0.183 72	0.185 61	0.186 25	0.186 36	0.186 36			-0.000 10	0.187 052 7
SiH	0.214 55	0.216 41	0.217 41	0.217 61	0.217 61			-0.000 06	0.218 14
PH	0.248 69	0.250 42	0.251 80	0.252 23	0.252 23			-0.000 05	0.253 39
SH	0.276 22	0.277 74	0.278 65	0.279 22	0.279 23			-0.000 05	0.2799
HCl	0.303 44	0.304 88	0.305 32	0.305 94	0.305 95	0.305 93	0.305 88	-0.000 05	0.306 998 5
N ₂	0.016 97	0.017 03	0.016 82	0.017 22	0.017 29	0.017 31	0.017 29	0.000 00	0.017 318
O ₂	0.015 12	0.015 18	0.015 01	0.015 78	0.015 90			0.000 00	0.015 930 5
F ₂	0.012 44	0.012 44	0.012 25	0.012 59	0.012 60	0.012 64	0.012 63	0.000 00	0.012 595 2
Si ₂	0.001 28	0.001 30	0.001 30	0.001 34	0.001 34			0.000 00	0.001 35
P ₂	0.001 42	0.001 43	0.001 41	0.001 46	0.001 47	0.001 48		0.000 00	0.001 49
S ₂	0.001 53	0.001 55	0.001 54	0.001 59	0.001 59			0.000 00	0.001 597 54
Cl ₂	0.001 45	0.001 45	0.001 45	0.001 47	0.001 47	0.001 48		0.000 00	0.001 516
BF	0.018 88	0.019 01	0.019 05	0.019 06	0.019 06			0.000 00	0.019 048 48
CO	0.017 33	0.017 41	0.017 37	0.017 54	0.017 52	0.017 52	0.017 50	0.000 00	0.017 505 13
BCl	0.006 67	0.006 74	0.006 77	0.006 79	0.006 79			0.000 00	0.006 812 4
CS	0.005 80	0.005 85	0.005 85	0.005 94	0.005 93	0.005 93		0.000 00	0.005 918 35
SiO	0.004 94	0.004 99	0.004 96	0.005 05	0.005 04			0.000 00	0.005 037 84
PN	0.005 34	0.005 37	0.005 28	0.005 47	0.005 50			0.000 00	0.005 533 7
SO	0.005 57	0.005 60	0.005 56	0.005 75	0.005 77			0.000 00	0.005 750 8
AlF	0.004 90	0.004 99	0.005 00	0.005 00	0.005 00			0.000 00	0.004 984 261
ClF	0.004 25	0.004 26	0.004 26	0.004 33	0.004 33			0.000 00	0.004 338 5
AlCl	0.001 59	0.001 61	0.001 61	0.001 62	0.001 62			0.000 00	0.001 611 082
SiS	0.001 43	0.001 45	0.001 45	0.001 48	0.001 47			0.000 00	0.001 473 13
Error statistics for hydrides (10 systems) ^c									
MSD	-0.005 14	-0.003 25	-0.002 14	-0.001 47	-0.001 46				
MAD	0.005 14	0.003 25	0.002 19	0.001 52	0.001 50				
RMSD	0.005 49	0.003 79	0.002 79	0.001 92	0.001 90				
Error statistics for nonhydrides (18 systems) ^c									
MSD	-0.000 16	-0.000 12	-0.000 16	-0.000 02	-0.000 01				
MAD	0.000 16	0.000 12	0.000 16	0.000 03	0.000 02				
RMSD	0.000 24	0.000 21	0.000 28	0.000 05	0.000 02				
Error statistics for everything (28 systems) ^c									
MSD	-0.001 94	-0.001 24	-0.000 87	-0.000 54	-0.000 53				
MAD	0.001 94	0.001 24	0.000 89	0.000 56	0.000 55				
RMSD	0.003 41	0.002 36	0.001 74	0.001 19	0.001 18				

^aDBOC correction at the HF/AVTZ level.^bFrom Ref. 69.^cSee footnote b of Table I.

characterized by moderate nondynamical correlation effects, $20 \leq \% \text{TAE}_e[\text{SCF}] \leq 60$ and $6 \leq \% \text{TAE}_e[(\text{T})] \leq 8$. Finally, C₂, BN, and O₃ are pathologically multireference: at the SCF level BN and O₃ are unbound, and only 10% of the atomization energy of C₂ is accounted for, while the (T) triples account for as much as 13%–19% of the binding energies of these systems.

B. Equilibrium geometries (r_e) of diatomic molecules

Table I compares the equilibrium bond distances obtained at the W4 (and related) levels with experimental bond

lengths for our set of 10 monohydride and 18 nonhydride diatomic molecules. The equilibrium bond lengths determined at the clamped-nuclei, frozen-core, nonrelativistic CCSD(T) basis set limit (W4 [up to CCSD(T)_{fc,nr}] method) almost universally overestimate the experimental bond distances (by ~ 0.3 pm on average). Inclusion of the core-valence and scalar relativistic corrections consistently reduces r_e by amounts ranging from ~ 0.1 pm (for HF, OH, F₂, and NH) to ~ 1.0 pm (for AlCl and Si₂). Consequently, at the clamped-nuclei, all-electron, relativistic CCSD(T) basis set limit (W4 [up to CCSD(T)] method) r_e are universally

TABLE VI. Spectroscopic constants (r_e in picometer, all the rest in cm^{-1}) for the 12-electron isoelectronic series C_2 , BN , and BeO obtained from a Dunham analysis of potential energy curves computed at the W4 and related levels. (For C_2 , BN , and BeO , DBOC contributions are found to be insignificant and are not included in the theoretical values.)

	W4 [up to CCSD(T) _{fc,nr.}]	W4 [up to CCSD(T)]	W4 [up to CCSDT]	W4 [up to CCSDTQ]	W4	W4 ^a	W4 ^{ab}	W4.2 ^{ab}	W4.3 ^b	Expt. ^c
$\text{C}_2 (X^1\Sigma_g^+)$										
r_e	124.40	124.04	124.00	124.19	124.21		124.22	124.22	124.22	124.2440
ω_e	1861.29	1872.11	1874.62	1859.09	1857.63		1857.43	1856.55	1855.84	1855.0142
$\omega_e x_e$	12.51	12.48	12.63	13.44	13.45		13.45	13.50	13.53	13.5547
$\omega_e y_e$	-0.020	-0.019	-0.039	-0.081	-0.082		-0.082	-0.083	-0.088	-0.1321
α_e	0.017 24	0.017 26	0.017 28	0.017 83	0.017 83		0.017 83	0.017 88	0.017 89	0.018 013
$\text{BN} (a^1\Sigma^+)$										
r_e	126.85	126.43	127.17	127.33	127.38	127.42	127.43	127.43	127.33	127.450 81
ω_e	1742.85	1755.27	1719.62	1713.06	1711.08	1707.50	1707.28	1707.64	1709.81	1705.4032
$\omega_e x_e$	16.33	16.08	12.29	11.99	11.76	11.40	11.40	11.37	11.68	10.553 38
$\omega_e y_e$	-0.505	-0.511	-0.004	-0.013	-0.015	-0.015	-0.015	-0.024	0.036	
α_e	0.016 69	0.016 63	0.016 65	0.016 38	0.016 27	0.016 18	0.016 17	0.016 11	0.016 32	0.013 857
$\text{BeO} (X^1\Sigma^+)$										
r_e	133.63	132.89	132.85	132.98	132.88	133.01	133.07	133.07		133.09
ω_e	1479.86	1497.59	1507.02	1494.41	1501.65	1493.43	1488.55	1488.55		1487.32
$\omega_e x_e$	12.05	12.14	10.95	12.12	12.34	11.78	11.69	11.66		11.83
α_e	0.018 89	0.019 00	0.018 10	0.018 93	0.018 89	0.018 81	0.018 84	0.018 82		0.0190

^aDiffuse functions are added to electronegative atoms (N and O) in all the valence post-CCSD(T) steps, see text.

^bThe inner-shell correlation contribution is extrapolated from RCCSD(T)/aug-cc-pwCVQZ and RCCSD(T)/aug-cc-pwCV5Z calculations, see text.

^c C_2 from Ref. 70, BN from Ref. 71, and BeO from Ref. 61.

underestimated (by ~ 0.2 pm on average). The largest underestimations are seen for the nonhydrides, e.g., by 0.26, 0.28, 0.31, 0.32, 0.33, 0.35, 0.38, 0.39, and 0.52 pm, for SiS , PN , ClF , Cl_2 , O_2 , S_2 , F_2 , P_2 , and Si_2 , respectively. For the subset of 18 nonhydride systems the W4 [up to CCSD(T)] method attains a RMSD of 0.27 pm. As expected, the performance for the subset of monohydride systems, which are mostly dominated by dynamical correlation ($0.1 \leq \% \text{TAE}[(\text{T})] \leq 1.6$), is much better with a RMSD of only 0.06 pm. For the entire set of 28 diatomics W4 [up to CCSD(T)] theory attains a RMSD of 0.22 pm.

Higher-order triple excitations $\hat{T}_3\text{-(T)}$ have a relatively small effect on the bond lengths: $|r_e|$ changes by ≤ 0.1 pm (with the exception of P_2 and PN for which r_e decreases by 0.2 pm). For the hydride systems the $\hat{T}_3\text{-(T)}$ contribution consistently increases the bond lengths by 0.01–0.06 pm, thereby improving the agreement with experiment. For the nonhydride systems the $\hat{T}_3\text{-(T)}$ excitations have a mixed effect, bettering agreement with experiment for some while worsening it for others. For the entire set of 28 diatomics, the effect of including the $\hat{T}_3\text{-(T)}$ contribution is manifested by a slight increase in the RMSD from 0.22 to 0.25 pm. Note that, with very few exceptions (namely BH , CH , and AlH), the W4 [up to CCSDT] method still universally underestimates the experimental bond lengths.

Connected quadruple excitations \hat{T}_4 universally increase the bond distances, thereby substantially improving the agreement with experiment, particularly for the nonhydride systems. Upon inclusion of the \hat{T}_4 excitations the RMSD over the nonhydrides is reduced from 0.30 to 0.06 pm (!), where in most cases the bond lengths increase by >0.2 pm (e.g., by 0.28, 0.29, 0.30, 0.33, 0.37, 0.42, and 0.46 for SO ,

S_2 , Si_2 , O_2 , PN , F_2 , and P_2 , respectively). For the monohydrides, the effect of the \hat{T}_4 excitations is rather modest, the bond lengths increasing by only 0.00–0.03 pm and the RMSD being reduced from 0.04 to 0.03 pm.

As expected, connected quintuple excitations have essentially no effect on the internuclear distances of the hydride systems. For the nonhydride systems the bond lengths generally increase by 0.00–0.05 pm upon inclusion of the \hat{T}_5 excitations.

At the full W4 level the RMSDs from experiment are {0.03, 0.05, 0.04} pm for the hydrides, nonhydrides, and the entire set, respectively. The largest deviations (underestimations) are 0.07 pm (for P_2 , SiH , SiS , and ClF) and 0.09 pm (for Cl_2).

The trends discussed above can be qualitatively understood by looking at how the various energy contributions ($E^{\text{core-valence}}$, $E^{\hat{T}_3\text{-(T)}}$, $E^{\hat{T}_4}$, and $E^{\hat{T}_5}$) change as a function of r . Tables SII–SV of the supporting information⁴⁶ give these energy contributions as a function of r . The said energy contributions (with the exception of $E^{\hat{T}_3\text{-(T)}}$ for BF and AlF ; *vide infra*) show a nearly linear dependence on r in the interval $|r - r_e| \leq 10$ pm. Addition of a linear term ($E \approx ar$) to a simple harmonic potential results in an increase in r_e if $a < 0$ and a decrease in r_e if $a > 0$. For all the systems, the connected quadruples energy contribution $E^{\hat{T}_4}$ decreases with r (in a nearly linear manner: $R^2 \geq 0.99$), and thereby inclusion of the \hat{T}_4 excitations universally lengthens the bond distances. The core-valence energy contribution $E^{\text{core-valence}}$ systematically increases with r (in a fairly linear fashion, $R^2 \geq 0.98$), thus universally shortening the bond lengths. For the hydride systems $E^{\hat{T}_3\text{-(T)}}$ decreases linearly with r ($R^2 \geq 0.98$), therefore lengthening the equilibrium bond lengths.

For the nonhydrides, the $E^{\hat{T}_3-(T)}$ energy contribution does not behave in a consistent manner: for some (namely, Si₂, Cl₂, BCl, ClF, AlCl, and SiS) it decreases with r therefore increasing r_e , while for others it increases with r , thus decreasing r_e . Interestingly, for the highly polar BF and AlF systems $E^{\hat{T}_3-(T)}$ varies quadratically with r in the scanned interval ($R^2 \geq 0.998$, see Table S-II of the supporting information⁴⁶) and r_e is not affected by the $\hat{T}_3-(T)$ correction. For most of the systems $E^{\hat{T}_5}$ decreases with r (exceptions are BF, BCl, AlF, AlCl, CS, SiS, and SiO), therefore inclusion of \hat{T}_5 excitations increases r_e for all but the said exceptions. In Sec. III C we shall see that the said energy contributions that increase r_e decrease ω_e and vice versa—as expected since $\omega \propto 1/r$.

For a few systems we were able to obtain potential curves at the W4.2 and W4.3 levels (see Table I). Adding the $\hat{T}_3-(T)$ correction to the core-valence contribution in W4.2 theory has little effect on the bond distances, namely, r_e is increased by 0.02 and 0.03 pm for F₂ and P₂, respectively. Likewise, computing all the valence post-CCSD(T) corrections with larger basis sets and adding a \hat{T}_6 correction in W4.3 theory increases the bond length of F₂ by merely 0.03 pm.

Finally, DBOC corrections universally increase the bond distances and, as expected, only have a perceptible effect on the hydride systems, something more pronounced for the lighter hydrides within each row. For example, the DBOC correction increases r_e by 0.06, 0.04, 0.03, 0.02, and 0.01 pm for the first-row hydrides BH, CH, NH, OH, and HF, respectively, and by 0.05, 0.04, 0.03, 0.02, and 0.01 pm for the second-row hydrides AlH, SiH, PH, SH, and HCl, respectively.

C. Harmonic frequencies (ω_e) of diatomic molecules

The harmonic frequencies at the W4 (and related) levels are given in Table II together with the experimental values. At the clamped-nuclei, all-electron, relativistic CCSD(T) basis set limit (W4 [up to CCSD(T)] method) the harmonic frequencies are universally overestimated by amounts ranging from ~ 1 cm⁻¹ (for AlF and AlCl) up to 29 cm⁻¹ (for O₂). Not surprisingly, the smallest errors (of 1–8 cm⁻¹) are observed for the systems for which %TAE_e(T) < 4 (see Sec. III A). The RMSDs of the W4 [up to CCSD(T)] method are {5.1, 11.2, 9.8} cm⁻¹ for the hydrides, nonhydrides, and the entire set, respectively.

For most systems W4 [up to CCSD(T)_{fc,nr}] and W4 [up to CCSD(T)] err on the same side of experiment, the exceptions are AlF, CO, BCl, CH, BF, and BH for which W4 [up to CCSD(T)_{fc,nr}] underestimates experiment by 2.5–8.6 cm⁻¹. We note that with few exceptions (namely BH, AlH, BF, AlF, CH, and SiH) W4 [up to CCSD(T)_{fc,nr}] is closer to experiment than W4 [up to CCSD(T)], as manifested in a RMSD for the entire set smaller by 2 cm⁻¹.

Higher-order triple excitations $\hat{T}_3-(T)$ consistently reduce the harmonic frequencies of the monohydride compounds by 1.4–5.0 cm⁻¹, thus cutting the RMSD for the monohydrides by almost 50% from 5.1 cm⁻¹ (W4 [up to

CCSD(T)] to 2.8 cm⁻¹ (W4 [up to CCSDT]). For the nonhydrides, the higher-order triple excitations have a mixed effect, reducing ω_e for some systems (e.g., by ~ 1 cm⁻¹ for Si₂, BCl, and Cl₂) and increasing ω_e for others (most notably by ~ 10 cm⁻¹ for N₂ and PN). In effect, the RMSD for the nonhydrides increases upon inclusion of the $\hat{T}_3-(T)$ correction (from 11.2 cm⁻¹ for W4 [up to CCSD(T)] to 15.2 cm⁻¹ for W4 [up to CCSDT]).

Connected quadruple excitations \hat{T}_4 universally reduce ω_e by amounts ranging from 0.0 to 5.0 cm⁻¹ for the monohydride systems and 0.3–31.5 cm⁻¹ for the nonhydride systems. The largest decreases of over 10 cm⁻¹ are seen for P₂, SO, F₂, N₂, PN, and O₂ (specifically by 13.4, 16.1, 16.7, 20.4, 21.8, and 31.5 cm⁻¹, respectively). Inclusion of the \hat{T}_4 excitations reduces the RMSD over the set of hydrides from 2.8 cm⁻¹ (W4 [up to CCSDT]) to 0.6 cm⁻¹ (W4 [up to CCSDTQ]), and over the set of nonhydrides from 15.2 cm⁻¹ (W4 [up to CCSDT]) to 2.4 cm⁻¹ (W4 [up to CCSDTQ]). Over the entire set of 28 diatomics the RMSD is reduced from 12.7 cm⁻¹ (W4 [up to CCSDT]) to 2.0 cm⁻¹ (W4 [up to CCSDTQ]), an improvement by nearly one order of magnitude (!). This clearly demonstrates that connected quadruple excitations are essential for obtaining the harmonic frequencies with near-spectroscopic accuracy.

As expected, connected quintuple excitations \hat{T}_5 have little or no effect for the hydrides: the biggest changes are seen for OH and HF for which ω_e is reduced by merely 0.1 cm⁻¹. For the nonhydrides \hat{T}_5 excitations change ω_e by up to 4 cm⁻¹. The biggest changes are observed for N₂, PN, and O₂, namely, ω_e is reduced by 3.3, 3.5, and 4.0 cm⁻¹, respectively.

Upon inclusion of the \hat{T}_5 excitations the RMSDs for the nonhydrides (and for the entire set) are reduced by 50%, thus at the W4 level RMSDs of {0.6, 1.2, 1.0} cm⁻¹ are obtained for the hydrides, nonhydrides, and the entire set, respectively. The largest deviation being 2.1 cm⁻¹ for F₂ and P₂. We note that these errors drop to 0.9 and 1.3 cm⁻¹, respectively, upon adding the $\hat{T}_3-(T)$ correction to the core-valence contribution in W4.2 theory. The error for F₂ is further reduced to 0.5 cm⁻¹ by upgrading the valence post-CCSD(T) corrections and adding a \hat{T}_6 correction in W4.3 theory.

Finally, a word is due on the effect of the DBOC correction on the harmonic frequencies. For the monohydride systems the DBOC reduces ω_e across the board, again more appreciably so for the lighter hydrides within each row. Specifically, the DBOC reduces ω_e by 2.1, 1.8, 1.4, 0.9, and 0.3 cm⁻¹ for the first-row hydrides BH, CH, NH, OH, and HF, respectively, and by 1.1, 1.0, 0.9, 0.7, and 0.5 cm⁻¹ for the second-row hydrides AlH, SiH, PH, SH, and HCl, respectively. For the nonhydrides the DBOC negligibly increases the harmonic frequencies by <0.01 cm⁻¹, the biggest change of +0.08 cm⁻¹ being found for O₂.

D. First anharmonicity constant ($\omega_e x_e$) of diatomic molecules

Table III lists the theoretical and experimental first anharmonicity constants. Monohydrides are well known to ex-

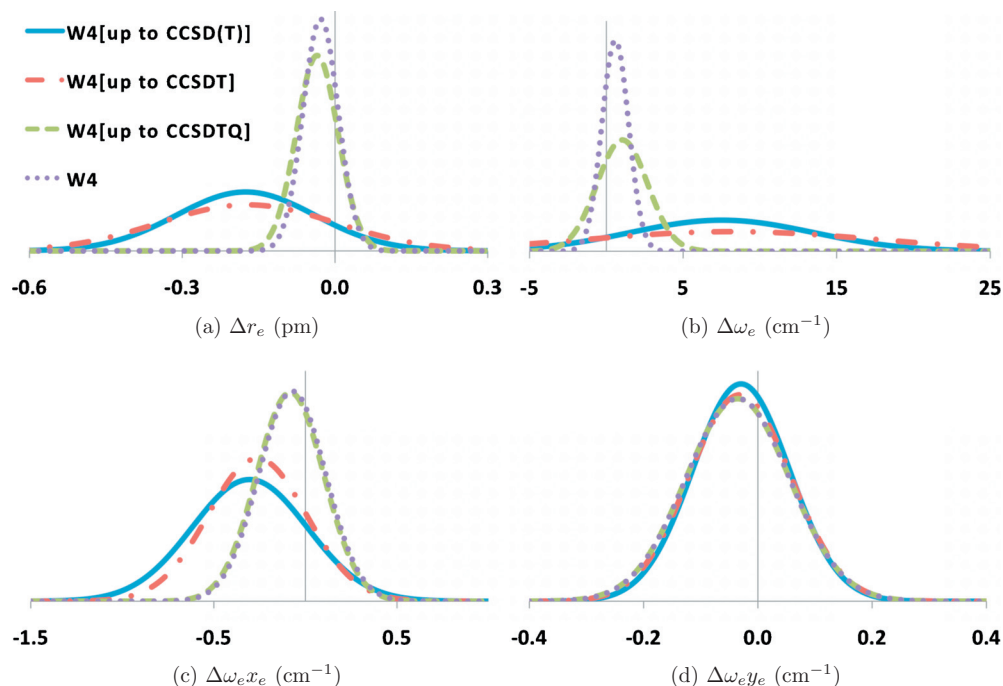


FIG. 1. Normal distribution of errors between theory and experiment for r_e , ω_e , $\omega_e x_e$, and $\omega_e y_e$. The centers of the Gaussians for the W4 [up to CCSD(T)], W4 [up to CCSDT], W4 [up to CCSDTQ], and W4 methods, respectively, are given in parenthesis: (a) equilibrium bond lengths (-0.16 , -0.17 , -0.04 , and -0.03 pm), (b) harmonic frequencies (7.5 , 8.1 , 1.0 , and 0.6 cm^{-1}), (c) first-order anharmonic corrections (-0.30 , -0.26 , -0.08 , and -0.07 cm^{-1}), and (d) second-order anharmonic corrections (-0.03 , -0.03 , -0.04 , and -0.04 cm^{-1}).

hibit relatively strong anharmonicity effects: $\omega_e x_e$ ranges between 30 and 90 cm^{-1} for the subset of monohydrides, and between 2 and 14 cm^{-1} for the subset of nonhydrides.

The W4 [up to CCSD(T)] method almost universally underestimates $\omega_e x_e$ by amounts ranging from 0.01 cm^{-1} (BF) to 1.0 cm^{-1} (NH). At this level RMSDs of $\{0.6, 0.3, 0.5\}$ cm^{-1} are obtained for the hydrides, nonhydrides, and the entire set, respectively. We note that the W4 [up to CCSD(T)_{fc,nr}] method shows very similar performance for most of the systems, the core-valence correction tends to slightly increase $\omega_e x_e$ but overall offers little improvement.

Inclusion of higher-order triple excitations improves the agreement with experiment for the monohydride systems, and slightly worsens the agreement with experiment for the nonhydride systems. For the monohydride systems \hat{T}_3 -(T) excitations increase $\omega_e x_e$ by up to 0.5 cm^{-1} (for NH), whereas for the nonhydrides they tend to decrease $\omega_e x_e$ by up to 0.3 cm^{-1} (for N_2 and F_2). The RMSD of the W4 [up to CCSDT] method is 0.4 cm^{-1} for both the hydride and nonhydride subsets.

Inclusion of connected quadruple excitations in the W4 [up to CCSDTQ] method universally increases $\omega_e x_e$ by up to 1.0 cm^{-1} . Thus, improving the agreement with experiment across the board, something more pronounced for the nonhydride systems. The largest improvements are seen for N_2 and O_2 : the error for N_2 is reduced from 0.7 to 0.2 cm^{-1} , and that for O_2 from 1.1 to 0.1 cm^{-1} .

Contributions from connected quintuple excitations are generally negligible (for most of the systems <0.01 cm^{-1}), the largest changes being +0.06, +0.11, and +0.15 cm^{-1} for PN, N_2 , and O_2 , respectively.

For the nonhydride systems the agreement between W4

and experiment is as good as one can hope for with a RMSD of 0.04 cm^{-1} . For the hydride systems the RMSD is almost one order of magnitude larger (0.32 cm^{-1}) but still well within the goal of “spectroscopic accuracy.”

W4.2 and W4.3 theories offer no significant improvement over W4 theory. Likewise, DBOC corrections are negligible (the largest correction of -0.02 cm^{-1} is obtained for BH).

E. Second anharmonicity constant ($\omega_e y_e$) of diatomic molecules

Table IV reports the theoretical and experimental second anharmonicity constants. The second-order anharmonicity constants are typically 2–3 orders of magnitude smaller than the first-order anharmonicity constants. For the monohydrides $\omega_e y_e$ ranges from 0.1 cm^{-1} (for SiH, PH, and SH) to 0.9 cm^{-1} (for HF). For the nonhydrides, which exhibit weaker anharmonicity effects, $\omega_e y_e$ are typically <0.01 cm^{-1} , and are given in Table S-VI of the supporting information. The W4 [up to CCSD(T)_{fc,nr}] method attains near-zero RMSD of 0.003, 0.09, and 0.06 cm^{-1} for the nonhydrides, hydrides, and the entire set, respectively. For both subsets core-valence, post-CCSD(T), and DBOC corrections have very little effect on the second anharmonicity constants.

Figure 1 shows the normal distribution functions for the errors between the theoretical and experimental r_e , ω_e , $\omega_e x_e$, and $\omega_e y_e$. It illustrates that r_e and ω_e are much more sensitive to post-CCSD(T) correlation effects, in particular to the \hat{T}_4 excitations, than the anharmonic corrections. This was suggested long ago, based on CEPA (Ref. 47) calculations on the methane surface by Pulay and co-workers.⁴⁸ The Gaussians

for the W4 [up to CCSDT] and W4 [up to CCSDTQ] methods are centered, respectively, around -0.17 and -0.04 pm for r_e , around 8.1 and 1.0 cm^{-1} for ω_e , around -0.3 and -0.1 cm^{-1} for $\omega_e x_e$, and around -0.03 and -0.04 cm^{-1} for $\omega_e y_e$.

F. Vibration-rotation coupling constant (α_e) of diatomic molecules

Table V depicts the theoretical and experimental vibration-rotation coupling constants. The RMSDs of the W4 [up to CCSD(T)_{fc,nr}], W4 [up to CCSD(T)], W4 [up to CCSDT], W4 [up to CCSDTQ], and W4 methods are 0.0034, 0.0024, 0.0017, 0.0012, and 0.0012 cm^{-1} , respectively. Hence it can be concluded that while the α_e are reasonably well converged at the clamped-nuclei, frozen-core, nonrelativistic CCSD(T) basis set limit (W4[CCSD(T)_{fc,nr}] method), significant improvements can still be obtained beyond it.

G. Difficult eight-valence electron systems: C₂, BN, and BeO

The low-lying $^1\Sigma^+$ electronic states of the 12-electron isoelectronic diatomics C₂, BN, and BeO are known to have significant contributions from singly and doubly excited determinants, and thus represent an extremely challenging test for single reference electron correlation methods.⁴³ Table VI lists the spectroscopic constants at the W4 (and related) levels together with the experimental values. The harmonic frequencies are severely overestimated at the W4 [up to CCSD(T)] level, specifically by 17, 50, and 10 cm^{-1} for C₂, BN, and BeO, respectively. Higher-order triples \hat{T}_3 -(T) contributions increase the errors for C₂ and BeO to about 20 cm^{-1} , but reduce the error for BN by 36 cm^{-1} (!) to 14 cm^{-1} . (Interestingly, the same decrease of 36 cm^{-1} was computed nearly two decades ago by one of us using a double zeta quality basis set.⁸) As expected, connected quadruple excitations reduce ω_e by substantial amounts, namely, 15.5, 6.6, and 12.6 cm^{-1} for C₂, BN, and BeO, respectively. Note, however, that for BN the \hat{T}_4 excitations have a lesser effect on ω_e than the \hat{T}_3 -(T) excitations. \hat{T}_5 excitations further reduce the errors for C₂ and BN by 1.5 and 2.0 cm^{-1} , respectively, but increase the error for BeO by 7.2 cm^{-1} . Thus, at the W4 level the harmonic frequencies of C₂, BN, and BeO are overestimated by 2.6, 5.7, and 14.3 cm^{-1} , respectively.

We suspected that the large discrepancies seen for the ionic BN and BeO molecules are partly due to the difficulty of the unaugmented basis sets to describe the charge distribution in the valence post-CCSD(T) steps. Adding diffuse functions on the electronegative atoms (N and O) in all the valence post-CCSD(T) steps in W4 theory (see computational methods section and footnote a in Table VI) reduces the errors for BN and BeO to 2.1 and 6.1 cm^{-1} , respectively. In addition, because of the fairly small core-valence gap in BeO, we also considered extrapolating the CCSD(T) inner-shell correlation contribution from larger basis sets (see computational methods section and footnote b in Table VI),

which results in further reduction of the error for BeO to 1.2 cm^{-1} . (The reduction to 1.9 cm^{-1} for BN is not significant.)

As mentioned in Sec. III B, the W4 [up to CCSD(T)] method consistently underestimates the experimental bond lengths of the diatomic molecules in Table I (by ~ 0.2 pm on average). Similarly, the bond distances of C₂ and BeO are underestimated by 0.2 pm, but that of BN is underestimated by as much as 1.0 pm. Higher-order triples \hat{T}_3 -(T) have little effect on r_e of C₂ and BeO, but increase r_e of BN by as much as 0.7 pm (!) narrowing the gap between theory and experiment to 0.3 pm. \hat{T}_4 contributions further reduce the discrepancy between theory and experiment: W4 [up to CCSDTQ] underestimates the experimental bond lengths of C₂, BN, and BeO by 0.05, 0.12, and 0.11 pm, respectively. \hat{T}_5 excitations increase r_e of C₂ and BN by 0.03 and 0.05 pm, but decrease r_e of BeO by 0.11 pm. Thus, at the W4 level the C₂ and BN bond lengths are in relatively good agreement with experiment (underestimating by 0.03 and 0.07 pm, respectively), but r_e of BeO is underestimated by as much as 0.21 pm. Again, augmenting the basis sets on N and O in all the valence post-CCSD(T) steps in W4 theory reduces the discrepancy for BeO to 0.08 pm, and for BN to 0.03 pm. Extrapolating the inner-shell correlation from RCCSD(T)/aug-cc-pwCVQZ and RCCSD(T)/aug-cc-pwCV5Z calculations results in further reduction of the error for BN and BeO to merely 0.02 pm.

Turning our attention to the first anharmonicity constants, for C₂ errors of 1.1 and 0.1 cm^{-1} are obtained at the W4 [up to CCSD(T)] and W4 levels, where the biggest improvement comes from the \hat{T}_4 excitations (see Table VI). For BN errors of 5.5 and 1.2 cm^{-1} are obtained at the W4 [up to CCSD(T)] and W4 levels, but here the improvement essentially stems from the \hat{T}_3 -(T) contribution. For BeO errors of 0.3 and 0.5 cm^{-1} are obtained at the W4 [up to CCSD(T)] and W4 levels. We note that by adding diffuse functions on N and O in all the post-CCSD(T) steps in W4 theory the errors for BN and BeO are further reduced to 0.85 and 0.05 cm^{-1} , respectively.

H. Triatomic systems

The W4 equilibrium geometries, harmonic frequencies, and fundamental frequencies of H₂O, CO₂, and O₃ are given in Table VII together with the available experimental values. The W4 equilibrium geometries are in close agreement with the experimental ones. The equilibrium bond distances of CO₂ and O₃ are both 0.02 pm lower than the experiment, and the bond angle of O₃ is 0.07° higher than that of Barbe *et al.*⁴⁹ For H₂O the W4 bond distance (95.76 pm) is bracketed in between the experimental value of Benedict *et al.*⁵⁰ (95.72 pm) and the more recent value of Jensen⁵¹ (95.84 pm), and the W4 bond angle (104.50°) is in between the said experimental values [104.52° (Ref. 50) and 104.44° (Ref. 51), respectively]. The Born–Oppenheimer correction is expected to be negligible for CO₂ and O₃, and is on the order of 0.003 pm and 0.02° for the bond distance and bond angle of water, respectively.⁵² We note that our W4 r_e and θ_e for water differ

TABLE VII. Theoretical and experimental equilibrium geometries, harmonic frequencies, and fundamental frequencies (in picometer, degrees, and cm^{-1}) for H_2O , CO_2 , and O_3 . (All the theoretical frequencies are computed at the W4-optimized geometries; unless otherwise indicated the DBOC contributions are not included in the theoretical values, cf. footnote b.)

	r_e	θ_e	ω_1	ω_2	ω_3	ν_1	ν_2	ν_3	Ref.
CO_2									
W4	115.98		1351.9	670.5	2396.4	1331.5	666.4	2350.2	
Expt.	116.00		1353.8	672.9	2396.5	1332.9	672.9	2349.1	72
H_2O									
W4	95.76	104.50	3834.6	1648.3	3945.7	3655.8	1595.3	3754.3	
W4 ^a			3835.2	1648.0	3946.3	3656.4	1595.2	3755.0	
Expt.	95.72	104.52	3832.2	1648.5	3942.5				50
Expt.	95.84	104.44	3831.8	1647.8	3942.4				51
Expt.						3657.1	1594.7	3755.9	73
O_3									
W4 [up to CCSDT]			1153.6	717.9	1085.7	1126.5	704.9	1042.1	
W4 [up to CCSDTQ]			1137.0	715.5	1070.2	1105.3	701.5	1020.3	
W4	127.15	116.82	1133.9	715.2	1067.1	1100.4	701.5	1016.0	
W4* ^b					1078.1				
Expt.	127.17	116.78	1134.9	716.0	1089.2				74
Expt.	127.17	116.75	1133.3	715.0	1087.3				49

^aIncluding a DBOC correction at the HF/aug'-cc-pVTZ level of theory.

^bW4* = W4[up to CCSDT] + $\hat{T}_4/\text{cc-pVTZ}(\text{no } f \ 1d)$ + $\hat{T}_5/\text{cc-pVDZ}(\text{no } d)$, see text.

by 0.02 pm and 0.02°, respectively, from the *ab initio* Born–Oppenheimer geometry reported in Ref. 52.

The W4 harmonic frequencies for CO_2 and H_2O are in relatively good agreement with experiment. In particular, the symmetric, bending, and antisymmetric vibrational frequencies of CO_2 underestimate the experimental values by 1.9, 2.4, and 0.1 cm^{-1} , respectively, and those of H_2O overestimate experiment⁵¹ by 2.8, 0.5, and 3.3 cm^{-1} , respectively.

Ozone represents an extremely challenging system for both single reference and multireference methods (see, e.g., Refs. 53–55 and references therein). The theoretical symmetric stretch converges smoothly with the level of theory, i.e., it overestimates the experimental value of Barbe *et al.*⁴⁹ by 20.3, 3.7, and 0.6 cm^{-1} , respectively, at the W4 [up to CCSDT], W4 [up to CCSDTQ], and W4 levels. The harmonic bending frequency converges more rapidly, in particular it overestimates the experimental one by 2.9, 0.5, and 0.2 cm^{-1} at the same levels, respectively. However, the asymmetric stretch (ω_3), which exhibits severe nondynamical correlation character,^{56–58} behaves in a less systematic manner. It underestimates the experimental value by 1.6, 17.1, and 20.2 cm^{-1} , respectively, at the said sequence of levels (where the good agreement between the W4 [up to CCSDT] value and experiment is clearly fortuitous). It is likely that the counterintuitive deterioration in agreement with experiment upon inclusion of the connected quadruple excitations is due to basis set deficiencies. The hypersensitivity of ω_3 to the treatment of connected quadruple excitations has been noted in Ref. 58. Determination of ω_3 requires evaluation of the energy at only one point (in C_s symmetry) aside from the equilibrium C_{2v} structure. We were able to obtain the CCSDTQ/cc-pVTZ (no $f \ 1d$) energies at these two points—cc-pVTZ (no $f \ 1d$) denotes the *sp* part of the cc-pVTZ basis set combined with the *d* function from the cc-pVDZ basis set. Replacing the \hat{T}_4 term in W4 theory with

$\hat{T}_4/\text{cc-pVTZ}(\text{no } f \ 1d)$ results in an asymmetric stretch of 1078.1 cm^{-1} , i.e., the error from experiment is reduced by more than 50%. Additionally upgrading the basis set for the parenthetical connected quadruple excitations to cc-pVTZ [i.e., $\hat{T}_4 = \text{CCSDT}(\text{Q})/\text{cc-pVTZ} - \text{CCSDT}/\text{cc-pVTZ} + \text{CCSDTQ}/\text{cc-pVTZ}(\text{no } f \ 1d) - \text{CCSDT}(\text{Q})/\text{cc-pVTZ}(\text{no } f \ 1d)$] results in a minor lowering of the asymmetric stretch by $\sim 1 \text{ cm}^{-1}$, and a further improvement in the basis set to the cc-pVQZ (no $g \ 1f$) basis set has a similar effect. Unfortunately, carrying out the fully iterative CCSDTQ/cc-pVTZ calculations is beyond the capabilities of our current computational resources, these calculations involving 5×10^9 and 10.5×10^9 amplitudes in C_{2v} and C_s symmetries, respectively.

It is appropriate to note, at this point, that—in spite of the difficulties the potential energy surface of ozone presents for W4 theory—W4 performs very well for the thermochemistry of O_3 . In particular, the post-CCSD(T) components are practically converged at the W4 level, as evident from very small differences between W4 and W4.3 theories. The post-CCSD(T) contributions to the total atomization energy of ozone in W4 and W4.3 theories are $\hat{T}_3 - (\text{T}) = -1.34$ and -1.37 ; $\hat{T}_4 = 3.81$ and 3.84; and $\hat{T}_5 = 0.41$ and 0.43.⁵⁹ In addition, W4.3 includes a \hat{T}_6 contribution of 0.05 kcal/mol. This suggests that while basis set convergence is faster for second-order properties (e.g., frequencies) than for the energy, *n*-particle treatment convergence is arguably slower.

I. Electrical properties

Fairly accurate experimental dipole moments are available for some of the molecules considered in the present work; however, for the higher-order properties (α and β) accurate experimental data are much more scarce. Furthermore, direct comparison between theory and experiment is

TABLE VIII. Dipole moments (in a.u., 1 a.u.=2.5416 D).

	W4 [up to CCSD(T) _{fc,nr}]	W4 [up to CCSD(T)]	W4 [up to CCSDT]	W4 [up to CCSDTQ]	W4	Expt.	Ref.
BH	0.550	0.552	0.551	0.551		0.50	61
HF	0.709	0.709	0.709	0.709	0.709	0.7185 ^a	61
HCl	0.433	0.430	0.429	0.429	0.429	0.4362 ± 0.0001	75
CO	0.044	0.046	0.044	0.048	0.049	0.0432	61
CS	0.774	0.777	0.771	0.774	0.778	0.770	61
BeO	2.496	2.484	2.469	2.470	2.484	2.2680	61
BN	0.796	0.796	0.850	0.811	0.799		
H ₂ O	0.729	0.730	0.730	0.729	0.729	0.730 ± 0.002	75
O ₃	0.218	0.218	0.222	0.214	0.213	0.2100	75
MSD ^b	0.035	0.034	0.031	0.031	0.033		
MAD ^b	0.038	0.038	0.035	0.035	0.038		
RMSD ^b	0.083	0.079	0.074	0.074	0.079		
MSD ^c	0.001	0.000	0.004	-0.001			
MAD ^c	0.004	0.002	0.010	0.004			
RMSD ^c	0.005	0.002	0.018	0.006			

^aReference 76 gives 0.707 a.u.

^bError statistics with respect to experiment.

^cError statistics with respect to the W4 values.

hampered by the fact that the theoretical values correspond to the static limit, whereas the experimental values are generally frequency-dependent. Thus, we will not attempt to quantify the reliability of W4 theory against experimental data; our intent is rather to investigate the effects of core-valence and post-CCSD(T) contributions on the electrical properties.

Table VIII gives the theoretical and experimental dipole moments. Core-valence and post-CCSD(T) corrections have no noticeable effect on systems dominated by dynamical correlation effects, and relatively little effects on the strongly multireference systems. The dipole moments at the frozen-core, nonrelativistic CCSD(T) basis set limit (W4 [up to CCSD(T)_{fc,nr}] method) agree very well with the full W4 values (RMSD=0.005 a.u., and the largest deviation of 0.01 a.u. is seen for BeO). At the W4 [up to CCSD(T)] level, the RMSD from W4 is 0.002 a.u., while the largest error of 0.005 a.u. is found for O₃. Adding the higher-order triple excitations increases the errors for the nonhydrides: in particular, a dramatic increase is seen for BN (from -0.003 to 0.05 a.u.). We note that for BN, the \hat{T}_3 -(T) excitations raise μ by 0.05 a.u. and the \hat{T}_4 excitations reduce it by 0.04 a.u. At the W4 [up to CCSDTQ] level, the largest errors of -0.014 and +0.012 a.u. are seen for BeO and BN, respectively, and the RMSD from W4 is 0.06 a.u.

Table IX shows the theoretical polarizabilities together with the available experimental data. The RMSDs from the full W4 values are 2.6, 2.9, 0.5, and 0.2 a.u. for the W4 [up to CCSD(T)_{fc,nr}], W4 [up to CCSD(T)], W4 [up to CCSDT], and W4 [up to CCSDTQ] methods, respectively. However, for most of the systems in Table IX, the polarizabilities at the W4 [up to CCSD(T)_{fc,nr}] level agree to within 0.1 a.u. with the W4 values. The main exceptions are α_{zz} of BeO, and α_{zz} and α_{xx} of C₂, which are overestimated by as much as 1.5, 5.4, and 13.0 a.u., respectively. Upon excluding C₂ and BeO the RMSD of the W4 [up to CCSD(T)_{fc,nr}] method drops to 0.13 a.u. The W4 [up to CCSD(T)_{fc,nr}] and W4 [up to

CCSD(T)] methods show very similar performance. Inclusion of \hat{T}_3 -(T) excitations dramatically reduces the said errors for C₂ to 0.1 and 1.0 a.u., respectively, and the RMSD for the entire set drops to 0.5 a.u. Nevertheless, at this level errors of -1.0 and 2.1 a.u. are still seen for α_{xx} and α_{zz} of BeO, respectively. These are reduced to -0.3 and 1.0 a.u., respectively, by inclusion of the \hat{T}_4 excitations in the W4 [up to CCSDTQ] method.

Table X lists the theoretical W4 (and related) hyperpolarizabilities. Similar to the polarizabilities, for most systems, the first hyperpolarizabilities at the W4 [up to CCSD(T)_{fc,nr}] level agree with the W4 values to within 0.1 a.u. The main exceptions are O₃ (β_{yyz}) and CS (β_{zzz}); excluding these, the W4 [up to CCSD(T)_{fc,nr}] method attains a RMSD of 0.3 a.u. from the W4 values. Inclusion of the core-valence and relativistic contributions (in the W4 [up to CCSD(T)] method) reduces the said RMSD to 0.1 a.u., and inclusion of post-CCSD(T) excitations offers little improvement. Turning our attention to the more problematic systems, we note that at the W4 [up to CCSD(T)_{fc,nr}] level β_{zzz} of CS is ~ 3 a.u. removed from the W4 value and that core-valence and post-CCSD(T) corrections do not significantly affect this result. The W4 [up to CCSD(T)_{fc,nr}] method gives the wrong sign for the β_{yyz} component of O₃, i.e., it overestimates the W4 value by as much as ~ 9 a.u. Inclusion of \hat{T}_3 -(T) excitations reduces this error to ~ 2 a.u. and further inclusion of \hat{T}_4 excitations reduces the error to -0.2 a.u.

J. Conclusions

For a chemically diverse set of 28 first- and second-row diatomic molecules for which very accurate experimental spectroscopic constants are available, W4 theory is capable of spectroscopically accurate predictions. Specifically, the RMSDs from experiment are 0.04 pm for r_e , 1.03 cm⁻¹ for ω_e , 0.20 cm⁻¹ for $\omega_e x_e$, 0.10 cm⁻¹ for $\omega_e y_e$, and 0.001 cm⁻¹ for α_e .

TABLE IX. Static polarizabilities (in a.u., 1 a.u.=1.481 85 × 10⁻²⁵ cm³) [$\bar{\alpha}=\frac{1}{3}(\alpha_{xx}+\alpha_{yy}+\alpha_{zz})$].

		W4 [up to CCSD(T) _{fc,nr}]	W4 [up to CCSD(T)]	W4 [up to CCSDT]	W4 [up to CCSDTQ]	W4	Expt.	Ref.
BH	α_{xx}	20.87	20.78	20.78	20.77			
	α_{zz}	23.14	23.03	23.05	23.06			
	$\bar{\alpha}$	21.63	21.53	21.53	21.53			
HF	α_{xx}	5.15	5.14	5.14	5.14	5.14	5.08	^a
	α_{zz}	6.29	6.28	6.28	6.29	6.29	6.40	^a
	$\bar{\alpha}$	5.53	5.52	5.52	5.53	5.53	5.52 ^b	^a
HCl	α_{xx}	16.68	16.65	16.65	16.65	16.65		
	α_{zz}	18.32	18.30	18.30	18.30	18.30		
	$\bar{\alpha}$	17.23	17.20	17.20	17.20	17.20	17.39 ^c	77
CO	α_{xx}	11.85	11.81	11.80	11.81	11.81	11.86	78
	α_{zz}	15.42	15.38	15.36	15.40	15.42	15.51	78
	$\bar{\alpha}$	13.04	13.00	12.99	13.01	13.01	13.08	78
CS	α_{xx}	23.74	23.62	23.63	23.62	23.63		
	α_{zz}	37.93	37.81	37.79	37.87	37.85		
	$\bar{\alpha}$	28.47	28.35	28.35	28.37	28.37		
P ₂	α_{xx}	39.91	39.66	39.66	39.65	39.65		
	α_{zz}	67.86	67.69	67.77	67.52	67.68		
	$\bar{\alpha}$	49.23	49.00	49.03	48.94	49.00		
Cl ₂	α_{xx}	24.86	24.81	24.81	24.81	24.81	24.43	79
	α_{zz}	41.74	41.66	41.68	41.65	41.65	44.54	79
	$\bar{\alpha}$	30.48	30.43	30.44	30.43	30.43	31.11 ^d	79
H ₂ O	α_{xx}	9.20	9.18	9.18	9.18	9.18		
	α_{yy}	9.84	9.83	9.83	9.84	9.84		
	α_{zz}	9.48	9.47	9.47	9.48	9.48		
	$\bar{\alpha}$	9.50	9.49	9.49	9.50	9.50	9.642 ^e	77
CO ₂	α_{xx}	12.74	12.74	12.73	12.75	12.75		
	α_{zz}	26.55	26.55	26.51	26.57	26.61		
	$\bar{\alpha}$	17.34	17.34	17.32	17.36	17.37	17.51 ^f	77
N ₂	α_{xx}	10.19	10.15	10.15	10.16	10.16		
	α_{zz}	14.78	14.73	14.76	14.71	14.72		
	$\bar{\alpha}$	11.72	11.68	11.69	11.68	11.68	11.744 ^g	75
F ₂	α_{xx}	6.38	6.37	6.37	6.37	6.37		
	α_{zz}	12.34	12.32	12.36	12.26	12.26		
	$\bar{\alpha}$	8.37	8.35	8.36	8.33	8.33	8.38	80
C ₂	α_{xx}	36.88	38.68	22.86	23.82	23.86		
	α_{zz}	31.80	31.81	26.36	26.33	26.42		
	$\bar{\alpha}$	35.18	36.39	24.03	24.66	24.71		
BeO	α_{xx}	31.46	31.36	30.63	31.30	31.59		
	α_{zz}	33.39	33.05	34.01	32.91	31.90		
	$\bar{\alpha}$	32.10	31.92	31.76	31.84	31.70		
O ₃	α_{xx}	11.75	11.72	11.72	11.73	11.73		
	α_{yy}	31.26	31.27	31.03	30.81	30.74		
	α_{zz}	14.18	14.14	14.10	14.11	14.11		
	$\bar{\alpha}$	19.06	19.04	18.95	18.88	18.86	21.7	75
	RMSD ^h	0.72	0.72	0.01	0.01			
	MAD ^h	0.73	0.75	0.17	0.06			
	RMSD ^h	2.59	2.89	0.47	0.20			

^aExperimental value with zero-point vibrational corrections taken from Ref. 81.^bReference 75 gives $\bar{\alpha}=5.4$ and Ref. 77 gives $\bar{\alpha}=5.601$ a.u.^cReference 82 gives $\bar{\alpha}=17.55$ a.u.; Ref. 79 gives $\alpha_{xx}=16.13$, $\alpha_{zz}=21.12$, and $\bar{\alpha}=17.75$ a.u.^dReference 82 gives $\bar{\alpha}=31.1$ a.u.^eReference 75 gives $\bar{\alpha}=9.8$ a.u.^fReference 82 gives $\bar{\alpha}=17.7$ a.u., Ref. 79 gives $\bar{\alpha}=17.88$ a.u., and Ref. 75 gives $\bar{\alpha}=19.64$ a.u.^gReference 79 gives $\alpha_{xx}=9.79$, $\alpha_{zz}=16.06$, and $\bar{\alpha}=11.88$ a.u., and Ref. 82 gives $\bar{\alpha}=11.92$ a.u.^hError statistics with respect to the W4 values.

Core-valence and post-CCSD(T) contributions have little effect on $\omega_e x_e$ and α_e , and especially on $\omega_e y_e$. As for r_e and ω_e , higher-order triple excitations \hat{T}_3 -(T) improve the agreement with experiment for the monohydride systems, but their inclusion (in the absence of \hat{T}_4) generally worsens

the agreement with experiment for the nonhydride diatomics. For instance, upon inclusion of the \hat{T}_3 -(T) corrections the RMSD in ω_e reduces from 5.1 to 2.8 cm⁻¹ for the subset of monohydride systems, and increases from 11.2 to 15.2 cm⁻¹ for the subset of nonhydride systems.

TABLE X. Static hyperpolarizabilities (in a.u., 1 a.u.=8.6392×10⁻³³ cm⁴ statvolt⁻¹) [$\bar{\beta}=\frac{3}{5}(\beta_{xxz}+\beta_{yyz}+\beta_{zzz})$].

		W4 [up to CCSD(T) _{fc,nr}]	W4 [up to CCSD(T)]	W4 [up to CCSDT]	W4 [up to CCSDTQ]	W4
BH	β_{zzz}	21.81	22.39	22.05	22.16	
	β_{xxz}	69.95	68.92	68.88	69.06	
	$\bar{\beta}$	70.85	69.27	69.43	69.57	
HF	β_{zzz}	8.75	8.77	8.79	8.82	8.83
	β_{xxz}	1.03	1.03	1.04	1.05	1.05
	$\bar{\beta}$	6.49	6.50	6.52	6.55	6.55
HCl	β_{zzz}	9.77	9.78	9.81	9.81	9.81
	β_{xxz}	0.29	0.33	0.32	0.31	0.31
	$\bar{\beta}$	6.21	6.26	6.28	6.26	6.26
CO	β_{zzz}	28.63	28.45	28.32	28.67	28.5
	β_{xxz}	7.66	7.60	7.56	7.64	7.67
	$\bar{\beta}$	26.37	26.19	26.06	26.38	26.31
CS	β_{zzz}	15.95	15.22	15.62	15.90	12.81
	β_{xxz}	4.79	4.48	4.38	4.61	4.72
	$\bar{\beta}$	15.31	14.50	14.63	15.07	13.35
H ₂ O	β_{zzz}	11.86	11.90	11.90	11.96	11.96
	β_{xxz}	4.62	4.62	4.63	4.66	4.66
	β_{yyz}	9.48	9.51	9.53	9.56	9.56
	$\bar{\beta}$	15.58	15.62	15.64	15.70	15.70
O ₃	β_{zzz}	-17.32	-17.22	-17.40	-17.43	-17.44
	β_{xxz}	-3.61	-3.59	-3.61	-3.62	-3.63
	β_{yyz}	1.66	1.92	-5.32	-7.22	-7.04
	$\bar{\beta}$	-11.56	-11.33	-15.80	-16.96	-16.87
	MSD ^a	0.77	0.70	0.22	0.18	
	MAD ^a	0.77	0.70	0.32	0.20	
	RMSD ^a	2.26	2.26	0.81	0.75	

^aError statistics with respect to the W4 values.

Connected quadruple excitations \hat{T}_4 are essential to obtain r_e and ω_e with RMSD of ~ 0.05 pm and ~ 2 cm⁻¹, respectively. For example, inclusion of the \hat{T}_4 excitations reduces the RMSD in ω_e from 2.8 to 0.6 cm⁻¹ for the subset of monohydrides, and from 15.2 to 2.4 cm⁻¹ for the subset of nonhydrides. The RMSDs in r_e are reduced from 0.04 to 0.03 pm for the hydride subset, and from 0.30 to 0.06 pm for the nonhydride subset. Moreover, inclusion of \hat{T}_4 excitations results in systematic trends: namely, r_e universally increase (by up to 0.5 pm), ω_e universally decrease (by up to 31.5 cm⁻¹), and $\omega_e x_e$ universally increase (by up to 1.0 cm⁻¹).

Connected quintuple excitations \hat{T}_5 are of minor importance for r_e and $\omega_e x_e$, but are spectroscopically significant for ω_e . Inclusion of a CCSDTQ5/cc-pVDZ(no d) correction term cuts the RMSD in the harmonic frequencies for our set of 28 diatomic molecules by 50% from 2.0 to 1.0 cm⁻¹, practically all of the improvement being due to the nonhydride systems.

DBOC corrections result in systematic trends and are of importance mainly for r_e and ω_e of the hydride systems, something more pronounced for the lighter hydrides within each row. For example, for our set of monohydrides DBOC universally increases r_e by 0.06–0.01 pm and universally decreases ω_e by 2.1–0.3 cm⁻¹.

For the pathologically multireference systems (BeO and BN) obtaining near-spectroscopic accuracy requires (i) augmenting the correlation-consistent basis sets on N and O in the valence post-CCSD(T) steps in W4 theory, and (ii) ex-

trapolating the CCSD(T) inner-shell contribution in W4 theory from the aug-cc-pwCV{Q,5}Z basis set pair.

The present study also considers water, carbon dioxide, and ozone. The experimental geometries and harmonic frequencies (with the exception of the asymmetric mode of ozone) are reproduced relatively accurately at the W4 level. However, the asymmetric stretch of ozone, which exhibits severe nondynamical character, is underestimated by as much as 20 cm⁻¹ at the W4 level. This deviation is reduced by more than 50% when the connected quadruples \hat{T}_4 term in W4 theory is calculated with the cc-pVTZ(no f 1d) basis set.

We also calculated the dipole moments (μ), polarizabilities (α), and first hyperpolarizabilities (β). We find that (i) excluding the pathologically multireference systems, the post-CCSD(T) contributions are of little importance for these electrical properties; (ii) the core-valence and DBOC contributions are also of little importance in most cases; and (iii) that the sensitivity to post-CCSD(T) effects, particularly for systems with significant nondynamical correlation, increases with increasing order of derivative with respect to the static electric field, i.e., in the order $\mu < \alpha < \beta$.

ACKNOWLEDGMENTS

Research at Weizmann was funded by the Israel Science Foundation (Grant No. 709/05), the Helen and Martin Kimmel Center for Molecular Design, and the Weizmann Alter-

native Energy Research Initiative (AERI). J.M.L.M. is the incumbent of the Baroness Thatcher Professorial Chair of Chemistry and a member *ad personam* of the Lise Meitner-Minerva Center for Computational Quantum Chemistry.

- ¹J. M. L. Martin, T. J. Lee, P. R. Taylor, and J. P. François, *J. Chem. Phys.* **103**, 2589 (1995).
- ²J. M. L. Martin, *Chem. Phys. Lett.* **292**, 411 (1998).
- ³F. Pawłowski, A. Halkier, P. Jørgensen, K. L. Bak, T. Helgaker, and W. Klopper, *J. Chem. Phys.* **118**, 2539 (2003).
- ⁴T. A. Ruden, T. Helgaker, J. Gauss, P. Jørgensen, and J. Olsen, *J. Chem. Phys.* **121**, 5874 (2004).
- ⁵D. P. Tew, W. Klopper, M. Heckert, and J. Gauss, *J. Phys. Chem. A* **111**, 11242 (2007).
- ⁶M. Heckert, M. Kállay, and J. Gauss, *Mol. Phys.* **103**, 2109 (2005).
- ⁷M. Heckert, M. Kállay, D. P. Tew, W. Klopper, and J. Gauss, *J. Chem. Phys.* **125**, 044108 (2006).
- ⁸J. M. L. Martin, T. J. Lee, G. E. Scuseria, and P. R. Taylor, *J. Chem. Phys.* **97**, 6549 (1992).
- ⁹R. Shepard, G. S. Kedziora, H. Lischka, I. Shavitt, T. Müller, P. G. Szalay, M. Kállay, and M. Seth, *Chem. Phys.* **349**, 37 (2008).
- ¹⁰X. Huang and T. J. Lee, *J. Chem. Phys.* **129**, 044312 (2008); **131**, 104301 (2009); X. Huang, D. W. Schwenke, and T. J. Lee, *J. Chem. Phys.* **129**, 214304 (2008).
- ¹¹C. Michauk and J. Gauss, *J. Chem. Phys.* **127**, 044106 (2007).
- ¹²B. Mintz, T. G. Williams, L. Howard, and A. K. Wilson, *J. Chem. Phys.* **130**, 234104 (2009).
- ¹³N. J. DeYonker, T. R. Cundari, and A. K. Wilson, *J. Chem. Phys.* **124**, 114104 (2006).
- ¹⁴A. Tajti, P. G. Szalay, A. G. Császár, M. Kállay, J. Gauss, E. F. Valeev, B. A. Flowers, J. Vázquez, and J. F. Stanton, *J. Chem. Phys.* **121**, 11599 (2004).
- ¹⁵Y. J. Bomble, J. Vázquez, M. Kállay, C. Michauk, P. G. Szalay, A. G. Császár, J. Gauss, and J. F. Stanton, *J. Chem. Phys.* **125**, 064108 (2006).
- ¹⁶M. E. Harding, J. Vázquez, B. Ruscic, A. K. Wilson, J. Gauss, and J. F. Stanton, *J. Chem. Phys.* **128**, 114111 (2008).
- ¹⁷A. Karton, E. Rabinovich, J. M. L. Martin, and B. Ruscic, *J. Chem. Phys.* **125**, 144108 (2006).
- ¹⁸A. Karton, P. R. Taylor, and J. M. L. Martin, *J. Chem. Phys.* **127**, 064104 (2007).
- ¹⁹T. Helgaker, W. Klopper, and D. P. Tew, *Mol. Phys.* **106**, 2107 (2008).
- ²⁰B. Ruscic, R. E. Pinzon, M. L. Morton, G. von Laszewski, S. Bittner, S. G. Nijssure, K. A. Amin, M. Minkoff, and A. F. Wagner, *J. Phys. Chem. A* **108**, 9979 (2004); B. Ruscic, *Yearbook of Science and Technology (Annual Update to McGraw-Hill Encyclopedia of Science and Technology)* (McGraw-Hill, New York, 2004), pp. 3–7; B. Ruscic, R. E. Pinzon, M. L. Morton, N. K. Srinivasan, M.-C. Su, J. W. Sutherland, and J. V. Michael, *J. Phys. Chem. A* **110**, 6592 (2006).
- ²¹A. Karton, S. Parthiban, and J. M. L. Martin, *J. Phys. Chem. A* **113**, 4802 (2009).
- ²²D. Feller and K. A. Peterson, *J. Chem. Phys.* **126**, 114105 (2007).
- ²³W. Klopper, R. A. Bachorz, C. Hättig, and D. P. Tew, *Theor. Chem. Acc.* **126**, 289 (2010).
- ²⁴MOLPRO, a package of *ab initio* programs designed by H.-J. Werner and P. J. Knowles, Version 2009.1, R. Lindh, F. R. Manby, M. Schütz *et al.*
- ²⁵MRCC, a string-based general coupled cluster program suite written by M. Kállay; See also M. Kállay and P. R. Surján, *J. Chem. Phys.* **115**, 2945 (2001), as well as <http://www.mrcc.hu>.
- ²⁶CFOUR, a quantum chemical program package written by J. F. Stanton, J. Gauss, M. E. Harding, and 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. Jusélius, K. Klein, W. J. Lauderdale, D. A. Matthews, T. Metzroth, D. P. O'Neill, D. R. Price, E. Prochnow, K. Ruud, F. Schiffmann, S. Stopkowitz, M. E. Varner, 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>.
- ²⁷T. H. Dunning, *J. Chem. Phys.* **90**, 1007 (1989).
- ²⁸R. A. Kendall, T. H. Dunning, and R. J. Harrison, *J. Chem. Phys.* **96**, 6796 (1992).
- ²⁹T. H. Dunning, K. A. Peterson, and A. K. Wilson, *J. Chem. Phys.* **114**, 9244 (2001).
- ³⁰K. A. Peterson and T. H. Dunning, *J. Chem. Phys.* **117**, 10548 (2002).
- ³¹W. A. de Jong, R. J. Harrison, and D. A. Dixon, *J. Chem. Phys.* **114**, 48 (2001).
- ³²A. Karton and J. M. L. Martin, *Theor. Chem. Acc.* **115**, 330 (2006).
- ³³F. Jensen, *Theor. Chem. Acc.* **113**, 267 (2005).
- ³⁴W. Klopper, *Mol. Phys.* **99**, 481 (2001).
- ³⁵P. J. Knowles, C. Hampel, and H.-J. Werner, *J. Chem. Phys.* **99**, 5219 (1993); **112**, 3106(E) (2000).
- ³⁶J. D. Watts, J. Gauss, and R. J. Bartlett, *J. Chem. Phys.* **98**, 8718 (1993).
- ³⁷M. Douglas and N. M. Kroll, *Ann. Phys.* **82**, 89 (1974).
- ³⁸B. A. Hess, *Phys. Rev. A* **33**, 3742 (1986).
- ³⁹J. L. Dunham, *Phys. Rev.* **41**, 721 (1932); **41**, 713 (1932).
- ⁴⁰A. Ralston and P. Rabinowitz, *A First Course in Numerical Analysis* (Dover, New York, 2000), pp. 94–95 and 148–149.
- ⁴¹T. J. Lee and P. R. Taylor, *Int. J. Quantum Chem., Symp.* **23**, 199 (1989); T. J. Lee, J. E. Rice, G. E. Scuseria, and H. F. Schaefer III, *Theor. Chim. Acta* **75**, 81 (1989).
- ⁴²T. J. Lee, *Chem. Phys. Lett.* **372**, 362 (2003); M. L. Leininger, I. M. B. Nielsen, T. D. Crawford, and C. L. Janssen, *ibid.* **328**, 431 (2000); C. L. Janssen and I. M. B. Nielsen, *ibid.* **290**, 423 (1998); I. M. B. Nielsen and C. L. Janssen, *ibid.* **310**, 568 (1999).
- ⁴³J. D. Watts and R. J. Bartlett, *Int. J. Quantum Chem.* **52**, 195 (1994).
- ⁴⁴J. D. Watts, M. Urban, and R. J. Bartlett, *Theor. Chim. Acta* **90**, 341 (1995).
- ⁴⁵J. Zheng, Y. Zhao, and D. G. Truhlar, *J. Phys. Chem. A* **111**, 4632 (2007).
- ⁴⁶See supplementary material at <http://dx.doi.org/10.1063/1.3489113> for Tables SI–SVI.
- ⁴⁷For a review see R. Ahlrichs, *Comput. Phys. Commun.* **17**, 31 (1979).
- ⁴⁸P. Pulay, W. Meyer, and J. E. Boggs, *J. Chem. Phys.* **68**, 5077 (1978).
- ⁴⁹A. Barbe, A. Chichery, T. Cours, V. G. Tyuterev, and J. J. Plateaux, *J. Mol. Struct.: THEOCHEM* **616**, 55 (2002).
- ⁵⁰S. Benedict, N. Gailar, and E. K. Plyler, *J. Chem. Phys.* **24**, 1139 (1956).
- ⁵¹P. Jensen, *J. Mol. Spectrosc.* **128**, 478 (1988).
- ⁵²A. G. Császár, G. Czakó, T. Furtenbacher, J. Tennyson, V. Szalay, S. V. Shirin, N. F. Zobov, and O. L. Polyansky, *J. Chem. Phys.* **122**, 214305 (2005).
- ⁵³I. Ljubić and A. Sabljic, *Chem. Phys. Lett.* **385**, 214 (2004).
- ⁵⁴K. W. Sattelmeyer, H. F. Schaefer III, and J. F. Stanton, *Chem. Phys. Lett.* **378**, 42 (2003).
- ⁵⁵R. J. Bartlett and J. F. Stanton, in *Reviews in Computational Chemistry*, edited by K. B. Lipkowitz and D. B. Boyd (VCH, New York, 1994), Vol. 5, Chap. 2, p. 65.
- ⁵⁶T. J. Lee, W. D. Allen, and H. F. Schaefer III, *J. Chem. Phys.* **87**, 7063 (1987).
- ⁵⁷J. F. Stanton, W. N. Lipscomb, D. H. Magers, and R. J. Bartlett, *J. Chem. Phys.* **90**, 1077 (1989).
- ⁵⁸S. A. Kucharski and R. J. Bartlett, *J. Chem. Phys.* **110**, 8233 (1999).
- ⁵⁹The W4 values are taken from Ref. 17, and due to computational resources constraints the CCSDTQ-CCSDT(Q) difference in W4.3 theory is calculated with the *spd* part of the cc-pVTZ basis set instead of the regular cc-pVTZ basis set.
- ⁶⁰W. T. M. L. Fernando and P. F. Bernath, *J. Mol. Spectrosc.* **145**, 392 (1991).
- ⁶¹K. P. Huber and G. Herzberg, *Constants of Diatomic Molecules* (Van Nostrand Reinhold, New York, 1979).
- ⁶²J. B. White, M. Dulick, and P. F. Bernath, *J. Chem. Phys.* **99**, 8371 (1993).
- ⁶³M. Betrencourt, D. Boudjaadar, P. Chollet, G. Guelachvili, and M. Morillon-Chapey, *J. Chem. Phys.* **84**, 4121 (1986).
- ⁶⁴N. Ohashi, K. Kawaguchi, and E. Hirota, *J. Mol. Spectrosc.* **103**, 337 (1984).
- ⁶⁵R. S. Ram, P. F. Bernath, R. Engleman, Jr., and J. W. Brault, *J. Mol. Spectrosc.* **172**, 34 (1995).
- ⁶⁶J. K. G. Watson, *J. Mol. Spectrosc.* **45**, 99 (1973).
- ⁶⁷A. G. Maki, F. J. Lovas, and R. D. Suenram, *J. Mol. Spectrosc.* **91**, 424 (1982).
- ⁶⁸H. S. P. Müller, M. C. McCarthy, L. Bizzocchi, H. Gupta, S. Esser, H. Lichau, M. Caris, F. Lewen, J. Hahn, C. Degli Esposti, S. Schlemmer, and P. Thaddeus, *Phys. Chem. Chem. Phys.* **9**, 1579 (2007).
- ⁶⁹K. K. Irikura, *J. Phys. Chem. Ref. Data* **36**, 389 (2007).
- ⁷⁰M. Douay, R. Nietmann, and P. F. Bernath, *J. Mol. Spectrosc.* **131**, 250 (1988).
- ⁷¹R. S. Ram and P. F. Bernath, *J. Mol. Spectrosc.* **180**, 414 (1996).

- ⁷²J. L. Teffo, O. N. Sulakshina, and V. I. Perevalov, *J. Mol. Spectrosc.* **156**, 48 (1992).
- ⁷³S. V. Shirin, N. F. Zobov, R. I. Ovsyannikov, O. L. Polyansky, and J. Tennyson, *J. Chem. Phys.* **128**, 224306 (2008).
- ⁷⁴A. Barbe, C. Secroun, and P. Jouve, *J. Mol. Spectrosc.* **49**, 171 (1974).
- ⁷⁵D. R. Lide, *CRC Handbook of Chemistry and Physics*, 85th ed. (CRC, Boca Raton, FL/Taylor & Francis, London, 2004).
- ⁷⁶J. S. Muentzer and W. Klemperer, *J. Chem. Phys.* **52**, 6033 (1970).
- ⁷⁷M. A. Spackman, *J. Chem. Phys.* **94**, 1288 (1991).
- ⁷⁸K. K. Sunil and K. D. Jordan, *Chem. Phys. Lett.* **145**, 377 (1988).
- ⁷⁹J. O. Hirschfelder, C. F. Curtis, and R. B. Bird, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1954), p. 950.
- ⁸⁰G. C. Straty and B. A. Younglove, *J. Chem. Phys.* **57**, 2255 (1972).
- ⁸¹G. H. F. Diercksen and A. J. Sadlej, *J. Chem. Phys.* **75**, 1253 (1981).
- ⁸²N. J. Bridge and A. D. Buckingham, *Proc. R. Soc. London, Ser. A* **295**, 334 (1966).