High Level ab Initio Quantum Mechanical Predictions of Infrared Intensities

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Vibrational intensities associated with the infrared spectra of H_2O, C_2H_2, HCN, H_2CO, CH_4, and SiH_4 were theoretically predicted by applying ab initio quantum mechanical methods at seven different levels of theory. The self-consistent field, second-order Møller−Plesset perturbation method, configuration interaction with single and double excitations, double excitations coupled-cluster, quadratic configuration interaction including single and double excitations (QCISD), coupled-cluster with single and double excitations (CCSD), and CCSD with perturbative triple excitations [CCSD(T)] levels of theory were applied. The atomic orbital basis sets employed included frozen-core double-ζ (DZ), triple-ζ (TZ), DZ plus single polarization (DZP), TZ plus double polarization (TZ2P), TZ plus triple polarization (TZ3P), TZ2P augmented with one set of higher angular momentum functions [TZ2P(f,d)], TZ2P(f,d) with one set of diffuse functions [TZ2P(f,d)+diff], TZ3P augmented with two sets of higher angular momentum functions [TZ3P(2f,2d)], [TZ3P(2f,2d)] with two sets of diffuse functions [TZ3P(2f,2d)+2diff], split valence plus polarization [6-311G(d,p) and 6-311G(3d,3p)], split valence with added polarization and diffuse functions [6-311++G(d,p) and 6-311++G(3d,3p)], Dunning's correlation consistent polarized valence [cc-pVXZ (X = 2−5)] basis sets, as well as augmented correlation consistent polarized valence [aug-cc-pVXZ (X = 2−5)] basis sets. The theoretical infrared intensities predicted at the different levels of theory for the studied molecules were compared with available experimental data. To complete the analysis, the predicted equilibrium geometries, dipole moments and harmonic vibrational frequencies were also compared with experiment. Several highly correlated types of wave functions employing extended basis sets produce intensity values in very good agreement with experiment. The best overall agreement between theory and experiment for all properties studied was obtained from highly correlated wave functions [QCISD, CCSD, CCSD(T)] combined with Dunning's correlation consistent aug-cc-pVXZ (X = 3−5) basis sets.

I. Introduction

The present study aims at evaluating the capabilities of state-of-the-art ab initio electronic structure theory in quantitatively predicting several basic molecular properties, with special emphasis on intensities in the infrared spectra. The prediction of molecular properties by advanced quantum mechanical methods has proved of paramount importance for the different spectroscopic techniques. The possibility to estimate theoretically and with good accuracy the spectral parameters has affected profoundly the development of the respective fields. In vibrational spectroscopy, the interest toward deriving from experiment the potential force fields of molecules through quite complicated but still approximate semiclassical procedures is gradually fading in view of the straightforward evaluation of quite accurate force fields from ab initio quantum mechanical computations. The difficulties in assigning the numerous observed bands in a spectrum to particular vibrational modes have also been largely overcome with the aid of theoretically determined normal coordinates. In a previous study,[1] it was shown for a number of small molecules that highly correlated wave functions employing basis sets of medium size can produce estimates of vibrational frequencies within an average deviation of about 1% from the experimental values. The quantitative predictions of vibrational intensities have, however, turned out particularly difficult. The quantum mechanical evaluation of intensities in the infrared spectra has been discussed in a number of comprehensive studies and reviews[1−6] as well as in a recent book.[7] The results indicate that by applying more sophisticated treatments of electron correlation and larger basis sets, the agreement between theoretical predictions and experimental IR intensities may become quite good. It was shown[1] that a good balance between theoretical method and basis set quality in predicting IR intensities as well as geometrical parameters, dipole moments, and harmonic vibrational frequencies is achieved via TZ2P CCSD(T) and TZ(2df,2pd) CCSD(T) computations. The impact of level of theory and basis set employed over the quality of theoretical predictions for a number of ground-state properties of H_2CO was discussed in a comprehensive review of Bruna, Hachey, and Grein,[8] which covered the literature until 1996. At higher correlated levels of theory, IR intensity results for formaldehyde from QCISD/6-311++G(d,p) computations[9] were discussed together with the CCSD and CCSD(T) TZ2P(2df,2pd) data of Thomas, DeLeeuw, Vacek, Crawford, Yamaguchi, and Schaefer[1] mentioned earlier.

It should be remembered that the experimental error in the available gas-phase IR intensities is often at least 10% and includes in most cases anharmonic and band overlap effects. In addition, the accuracy of experimental intensities for weak bands may be poorer than for strong bands.

In the present study, we apply seven different levels of ab initio electronic structure theory in evaluating geometrical

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TABLE 1: Theoretical Predictions of the Total Energy (in hartree), Dipole Moment (in debye), Geometrical Parameters (bond length in Å, angle in degrees), Harmonic Vibrational Frequencies (In Cm^{-1}), and Infrared Intensities (in parentheses in Km mol^{-1}) for the H_2O Molecule

level of theory	energy	r_e	θ_e	μ_e	$\omega_{1,a_1}(I_1)$	$\omega_{2,a_1}(I_2)$	$\omega_{3,b_2}(I_3)$
DZ SCF	−76.011002	0.9514	112.52	2.5297	4028 (3.4)	1711 (135.8)	4204 (65.0)
TZ SCF	−76.021696	0.9498	112.60	2.5377	3963 (0.0)	1697 (144.0)	4128 (55.7)
DZP SCF	−76.046550	0.9455	106.29	2.1306	4151 (21.6)	1752 (106.2)	4269 (75.5)
TZ2P SCF	−76.061148	0.9401	106.36	1.9885	4139 (15.0)	1765 (99.1)	4238 (81.0)
TZ3P SCF	−76.061398	0.9404	106.11	1.9351	4117 (14.2)	1765 (97.7)	4216 (88.4)
TZ2P(f,d) SCF	−76.062579	0.9401	106.38	1.9853	4134 (16.3)	1746 (99.5)	4236 (83.3)
TZ2P(f,d)+diff SCF	−76.063478	0.9403	106.39	1.9885	4133 (17.2)	1743 (93.9)	4235 (90.1)
TZ3P(2f,2d) SCF	−76.063368	0.9400	106.29	1.9298	4123 (14.4)	1748 (96.9)	4224 (89.7)
TZ3P(2f,2d)+2diff SCF	−76.063895	0.9401	106.35	1.9389	4122 (15.2)	1746 (96.2)	4223 (93.1)
6-311G(d,p) SCF	−76.047012	0.9410	105.46	2.1377	4142 (17.7)	1750 (78.0)	4238 (57.2)
6-311++G(d,p) SCF	−76.053423	0.9411	106.22	2.1958	4145 (25.5)	1726 (85.6)	4247 (88.3)
6-311G(3d,3p) SCF	−76.054263	0.9399	105.77	1.8732	4131 (10.4)	1774 (96.3)	4226 (80.1)
6-311++G(3d,3p) SCF	−76.057635	0.9402	106.21	1.9744	4130 (14.9)	1757 (93.7)	4229 (88.6)
cc-pVDZ SCF	−76.027054	0.9463	104.61	2.0447	4114 (21.2)	1776 (80.7)	4212 (60.5)
aug-cc-pVDZ SCF	−76.041844	0.9436	105.93	1.9646	4130 (14.4)	1744 (93.2)	4238 (87.9)
cc-pVTZ SCF	−76.057770	0.9406	106.00	1.9878	4127 (14.6)	1753 (90.3)	4227 (75.2)
aug-cc-pVTZ SCF	−76.061203	0.9410	106.31	1.9394	4121 (15.1)	1745 (96.4)	4223 (92.3)
cc-pVQZ SCF	−76.065519	0.9396	106.22	1.9649	4131 (15.1)	1751 (93.7)	4230 (85.5)
aug-cc-pVQZ SCF	−76.066676	0.9398	106.33	1.9361	4128 (15.2)	1748 (96.4)	4229 (92.8)
cc-pV5Z SCF	−76.067783	0.9395	106.33	1.9570	4131 (15.7)	1748 (95.1)	4231 (90.7)
aug-cc-pV5Z SCF	−76.068009	0.9396	106.34	1.9358	4130 (15.1)	1748 (96.5)	4231 (92.7)
6-311G(d,p) MP2	−76.263972	0.9578	102.44	2.1967	3905 (6.2)	1667 (51.2)	4013 (33.5)
6-311++G(d,p) MP2	−76.274920	0.9595	103.45	2.2575	3885 (13.1)	1629 (57.2)	4003 (62.7)
6-311G(3d,3p) MP2	−76.294622	0.9580	103.91	1.9164	3844 (1.8)	1651 (70.4)	3960 (63.5)
6-311++G(3d,3p) MP2	−76.300136	0.9591	104.48	2.0179	3831 (5.5)	1626 (68.5)	3957 (70.7)
cc-pVTZ MP2	−76.318658	0.9591	103.50	2.0426	3855 (5.7)	1652 (64.5)	3975 (55.1)
aug-cc-pVTZ MP2	−76.328992	0.9614	104.11	1.9927	3822 (5.6)	1628 (71.7)	3948 (75.4)
cc-pVQZ MP2	−76.347639	0.9577	104.01	2.0156	3855 (6.5)	1643 (69.1)	3978 (68.3)
aug-cc-pvQZ MP2	−76.351919	0.9588	104.26	1.9859	3840 (6.1)	1632 (73.1)	3966 (78.3)
DZP CISD	−76.241985	0.9627	104.36	2.0940	3931 (6.6)	1685 (80.0)	4048 (35.9)
TZ2P CISD	−76.293615	0.9531	104.93	1.9398	3934 (6.1)	1701 (78.2)	4032 (52.6)
TZ3P CISD	−76.296945	0.9544	104.72	1.8659	3887 (4.9)	1681 (76.0)	3990 (57.5)
TZ2P(f,d) CISD	−76.315884	0.9532	104.70	1.9386	3935 (8.0)	1682 (78.7)	4037 (57.1)
TZ2P(f,d)+diff CISD	−76.317321	0.9536	104.69	1.9418	3930 (8.8)	1679 (72.6)	4034 (63.5)
TZ3P(2f,2d) CISD	−76.323852	0.9518	104.80	1.8643	3920 (6.1)	1684 (77.4)	4023 (63.2)
TZ3P(2f,2d)+2diff CISD	−76.324767	0.9520	104.88	1.8753	3915 (6.8)	1682 (76.6)	4018 (66.3)
6-311G(d,p) CISD	−76.262816	0.9543	103.03	2.0893	3954 (5.8)	1699 (54.1)	4043 (27.4)
6-311++G(d,p) CISD	−76.272106	0.9551	103.93	2.1662	3948 (11.2)	1668 (59.7)	4044 (51.5)
6-311G(3d,3p) CISD	−76.289995	0.9531	104.48	1.7853	3914 (2.7)	1689 (75.1)	4010 (54.1)
6-311++G(3d,3p) CISD	−76.294654	0.9536	105.00	1.9116	3911 (5.9)	1669 (73.0)	4014 (60.7)
cc-pVDZ CISD	−76.230089	0.9618	102.45	1.9905	3896 (6.3)	1707 (58.9)	3995 (26.9)
aug-cc-pVDZ CISD	−76.259043	0.9607	104.40	1.8875	3881 (4.5)	1662 (71.4)	3990 (56.2)
cc-pVTZ CISD	−76.313875	0.9537	104.17	1.9374	3932 (6.4)	1690 (69.5)	4031 (49.4)
aug-cc-pVTZ CISD	−76.322396	0.9548	104.77	1.8756	3916 (6.6)	1672 (77.0)	4018 (66.2)
cc-pVQZ CISD	−76.339299	0.9517	104.71	1.9178	3943 (7.5)	1684 (75.0)	4044 (62.2)
6-311G(d,p) CCD	−76.270350	0.9563	102.86	2.0850	3924 (4.7)	1692 (52.3)	4016 (25.3)
6-311++G(d,p) CCD	−76.279737	0.9572	103.76	2.1644	3917 (10.0)	1660 (58.0)	4019 (49.3)
6-311G(3d,3p) CCD	−76.298388	0.9556	104.31	1.7805	3876 (2.1)	1679 (73.6)	3977 (52.5)
6-311++G(3d,3p) CCD	−76.303159	0.9561	104.88	1.9091	3873 (5.1)	1658 (71.6)	3980 (59.2)
cc-pVTZ CCD	−76.323440	0.9563	103.99	1.9333	3892 (5.3)	1681 (67.6)	3995 (46.8)
aug-cc-pVTZ CCD	−76.332297	0.9579	104.49	1.8746	3869 (5.7)	1662 (75.2)	3976 (63.6)
cc-pVQZ CCD	−76.349627	0.9545	104.51	1.9151	3900 (6.5)	1673 (73.2)	4005 (59.6)
6-311G(d,p) QCISD	−76.271699	0.9574	102.72	2.0800	3901 (3.8)	1688 (50.8)	3995 (22.8)
6-311++G(d,p) QCISD	−76.281752	0.9959	103.65	2.1612	3889 (8.5)	1654 (56.2)	3992 (45.4)
6-311G(3d,3p) QCISD	−76.300405	0.9568	104.07	1.7654	3854 (1.2)	1676 (70.5)	3953 (47.1)
6-311++G(3d,3p) QCISD	−76.305392	0.9576	104.71	1.8979	3847 (3.8)	1654 (68.6)	3955 (53.3)
cc-pVTZ QCISD	−76.324884	0.9574	103.85	1.9259	3872 (4.2)	1678 (65.5)	3975 (42.5)
aug-cc-pVTZ QCISD	−76.334167	0.9591	104.35	1.8594	3847 (4.1)	1658 (72.4)	3953 (57.4)
cc-pVQZ QCISD	−76.351182	0.9556	104.35	1.9064	3879 (5.1)	1671 (70.7)	3984 (53.8)
DZP CCSD	−76.250243	0.9659	104.11	2.0888	3879 (4.7)	1674 (76.7)	4003 (30.8)
TZ2P CCSD	−76.303515	0.9565	104.68	1.9326	3878 (4.4)	1689 (74.9)	3981 (46.8)
TZ3P CCSD	−76.307011	0.9580	104.46	1.8544	3829 (3.2)	1668 (72.5)	3936 (51.2)
TZ2P(f,d) CCSD	−76.326703	0.9567	104.42	1.9309	3877 (6.0)	1670 (75.4)	3984 (50.6)
TZ2P(f,d)+diff CCSD	−76.328271	0.9573	104.40	1.9342	3871 (6.7)	1667 (69.0)	3979 (56.9)
TZ3P(2f,2d) CCSD	−76.334956	0.9554	104.51	1.8521	3860 (4.2)	1672 (73.8)	3966 (56.3)
TZ3P(2f,2d)+2diff CCSD	−76.335952	0.9557	104.60	1.8637	3853 (4.8)	1669 (73.0)	3961 (59.3)
cc-pVDZ CCSD	−76.238206	0.9649	102.18	1.9825	3846 (4.4)	1696 (56.2)	3950 (22.6)
aug-cc-pVDZ CCSD	−76.268633	0.9644	104.14	1.8752	3822 (2.9)	1649 (68.0)	3937 (50.4)
cc-pVTZ CCSD	−76.324557	0.9571	103.89	1.9269	3876 (4.5)	1678 (66.1)	3979 (43.3)
aug-cc-pVTZ CCSD	−76.333670	0.9588	104.43	1.8629	3853 (4.6)	1659 (73.3)	3959 (58.9)
cc-pVQZ CCSD	−76.350812	0.9553	104.40	1.9077	3885 (5.5)	1671 (71.4)	3989 (55.0)
DZP CCSD(T)	−76.253309	0.9669	103.93	2.0794	3862 (3.6)	1668 (74.3)	3987 (27.6)

TABLE 1: (Continued)

level of theory	energy	r_e	θ_e	μ_e	$\omega_{1,a_1}(I_1)$	$\omega_{2,a_1}(I_2)$	$\omega_{3,b_2}(I_3)$
TZ2P CCSD(T)	−76.310199	0.9589	104.43	1.9226	3841 (3.3)	1678 (72.2)	3946 (42.6)
TZ3P CCSD(T)	−76.314104	0.9606	104.21	1.8386	3788 (2.1)	1655 (69.4)	3899 (46.7)
TZ2P(f,d) CCSD(T)	−76.334271	0.9591	104.15	1.9206	3839 (4.7)	1659 (72.5)	3948 (46.2)
TZ2P(f,d)+diff CCSD(T)	−76.335999	0.9598	104.13	1.9236	3832 (5.2)	1656 (65.9)	3942 (52.4)
TZ3P(2f,2d) CCSD(T)	−76.343283	0.9580	104.26	1.8354	3817 (2.9)	1659 (70.7)	3927 (51.7)
TZ3P(2f,2d)+2diff CCSD(T)	−76.344377	0.9584	104.35	1.8475	3810 (3.4)	1656 (69.9)	3921 (54.7)
cc-pVDZ CCSD(T)	−76.241305	0.9663	101.91	1.9720	3822 (3.2)	1690 (53.9)	3928 (19.3)
aug-cc-pVDZ CCSD(T)	−76.273904	0.9665	103.94	1.8584	3787 (1.9)	1638 (65.5)	3905 (46.4)
cc-pVTZ CCSD(T)	−76.332217	0.9594	103.58	1.9150	3841 (3.2)	1669 (63.0)	3946 (39.0)
aug-cc-pVTZ CCSD(T)	−76.342326	0.9616	104.18	1.8453	3811 (3.2)	1646 (70.4)	3920 (54.4)
cc-pVQZ CCSD(T)	−76.359798	0.9579	104.12	1.8947	3844 (4.0)	1659 (68.2)	3951 (50.4)
expt.[a]		0.9572	104.5		3832	1649	3943
expt.[b]		0.9578	104.5				
expt.[c]				1.8473	(2.24)	(53.6)	(44.6)
expt.[d]					(2.2)	(63.9)	(48.2)
expt.[e]					(2.2)	(66.6)	(39.8)
expt.[f]					(2.5)	(71.9)	
expt.[g]					(2.98)	(64.0)	(43.3)

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parameters, equilibrium dipole moments, harmonic vibrational frequencies and infrared intensities for H_2O, CH_4, H_2CO, C_2H_2, HCN, and SiH_4. These molecules were chosen because of the relative wealth of experimental IR intensity data. It is of special interest to assess in a systematic way the quality of theoretical predictions by combining different levels of theory in terms of electron correlation consideration and basis set used. Recent years have marked the improved accuracy of molecular electronic structure descriptions by applying basis sets involving diffuse functions. It is of special interest also to assess the potential of families of basis sets which systematically approach completeness, such as the correlation consistent cc-pVXZ and aug-cc-pVXZ basis sets developed by Dunning and coworkers.[10−13] In view of the recent theoretical developments and increasing power of digital technology, it is important to establish appropriate levels of theory for quantitative predictions of vibrational spectral parameters together with other basic molecular properties.

II. Computations

Electronic wave functions typically begin from the restricted Hartree−Fock self-consistent field method (SCF).[14−16] Here, dynamical electron correlation is then accounted for by the second-order Møller−Plesset perturbation method (MP2),[17−19] configuration interaction with single and double excitations (CISD),[20−23] double excitations coupled-cluster (CCD),[24] quadratic configuration interaction including single and double excitations (QCISD),[25] coupled-cluster with single and double excitations (CCSD),[26−29] and CCSD with perturbative triple excitations [CCSD(T)][30,31] levels of theory. The atomic orbital basis sets employed included frozen-core double-ζ (DZ), triple-ζ (TZ), DZ plus single polarization (DZP), TZ plus double polarization (TZ2P), TZ plus triple polarization (TZ3P), TZ2P augmented with one set of higher angular momentum functions [TZ2P(f,d)], TZ2P(f,d) with one set of diffuse functions [TZ2P-(f,d)+diff], TZ3P augmented with two sets of higher angular momentum functions [TZ3P(2f,2d)], TZ3P(2f,2d) with two sets of diffuse functions [TZ3P(2f,2d)+2diff], split valence plus polarization [6-311G(d,p) and 6-311G(3d,3p)], split valence with added polarization and diffuse functions [6-311++G(d,p) and 6-311++G(3d,3p)], Dunning's correlation consistent polarized valence [cc-pVXZ (X=2−5)] basis sets as well as augmented correlation consistent polarized valence [aug-cc-pVXZ (X=2−5)] basis sets.[10−13] Full geometry optimizations of all structures were obtained by analytic restricted Hartree−Fock SCF, MP2, CISD, CCD, QCISD, CCSD, and CCSD(T) closed-shell gradient techniques. SCF and MP2 harmonic vibrational frequencies were obtained from analytic second derivatives of the energy. The CISD, CCD, QCISD, CCSD, and CCSD(T) correlated frequencies were obtained by central finite differences of analytic gradients. IR intensities were determined using the double (mechanical and electrical) harmonic approximation. The PSI[32] and Gaussian 94[33] program packages for quantum chemical computations were used.

III. Results and Discussion

In Tables 1−6, the theoretically determined ab initio total energies, bond lengths (r_e), valence angles (α_e), dipole moments (μ_e), harmonic vibrational frequencies (ω_i), and infrared intensities (I_i) for the six molecules studied are presented. Results for the SCF, MP2, CISD, CCD, QCISD, CCSD, and CCSD(T) levels of theory with different basis sets are presented together with the experimental results for the respective quantities. In Tables 7 and 8, the percentage error between theoretical and experimental bond lengths and bond angles for selected basis sets at the different levels of theory are given. Table 9 presents the percentage deviation between theoretical and experimental dipole moments. In Tables 10 and 11, the percentage error between theoretical and experimental harmonic vibrational frequencies for the six molecules studied are presented. As emphasized earlier, one of the objectives of the present study is to determine the effect of inclusion of diffuse functions in the basis sets on the quality of theoretical predictions. Therefore, Tables 7−11 provide comparisons of the accuracy of computations employing basis sets with and without diffuse functions at the different levels of theory. Table 12 gives a general view of the overall accuracy of infrared intensity predictions achieved in the present study.

TABLE 2: Theoretical Predictions of the Total Energy (in hartree), Geometrical Parameter (bond length in Å), Harmonic Vibrational Frequencies (in Cm^{-1}), and Infrared Intensities (in parentheses in Km mol^{-1}) for the CH_4 Molecule

level of theory	energy	r_e	$\omega_{1,a_1}(I_1)$	$\omega_{2,e}(I_2)$	$\omega_{3,t_2}(I_3)$	$\omega_{4,t_2}(I_4)$
DZ SCF	−40.185613	1.0834	3177 (0)	1698 (0)	3307 (179.4)	1506 (85.6)
TZ SCF	−40.189789	1.0811	3128 (0)	1693 (0)	3234 (131.4)	1496 (72.3)
DZP SCF	−40.206212	1.0859	3170 (0)	1668 (0)	3286 (128.9)	1453 (44.0)
TZ2P SCF	−40.213581	1.0813	3160 (0)	1675 (0)	3257 (116.4)	1459 (28.9)
TZ3P SCF	−40.213464	1.0819	3146 (0)	1671 (0)	3246 (113.7)	1455 (27.6)
TZ2P(f,d) SCF	−40.214037	1.0819	3149 (0)	1667 (0)	3249 (117.6)	1455 (28.9)
TZ2P(f,d)+diff SCF	−40.214052	1.0819	3149 (0)	1667 (0)	3249 (117.6)	1455 (29.0)
TZ3P(2f,2d) SCF	−40.214360	1.0818	3149 (0)	1666 (0)	3248 (113.8)	1453 (27.1)
TZ3P(2f,2d)+2diff SCF	−40.214373	1.0818	3149 (0)	1666 (0)	3248 (114.1)	1453 (27.2)
6-311G(d,p) SCF	−40.209012	1.0842	3151 (0)	1668 (0)	3254 (130.2)	1453 (35.2)
6-311++G(d,p) SCF	−40.209150	1.0843	3150 (0)	1667 (0)	3252 (125.8)	1453 (35.9)
6-311G(3d,3p) SCF	−40.211802	1.0820	3147 (0)	1672 (0)	3244 (113.6)	1455 (27.6)
6-311++G(3d,3p) SCF	−40.211856	1.0820	3147 (0)	1671 (0)	3244 (113.8)	1455 (28.3)
cc-pVDZ SCF	−40.198712	1.0908	3165 (0)	1648 (0)	3286 (103.2)	1433 (29.7)
aug-cc-pVDZ SCF	−40.199633	1.0894	3153 (0)	1638 (0)	3266 (116.3)	1424 (27.0)
cc-pVTZ SCF	−40.213466	1.0821	3148 (0)	1666 (0)	3246 (118.6)	1454 (28.1)
aug-cc-pVTZ SCF	−40.213703	1.0821	3148 (0)	1666 (0)	3246 (114.2)	1453 (27.7)
cc-pVQZ SCF	−40.216302	1.0815	3149 (0)	1667 (0)	3247 (116.0)	1454 (28.0)
cc-pV5Z SCF	−40.217048	1.0814	3150 (0)	1667 (0)	3248 (114.3)	1454 (27.8)
aug-cc-pV5Z SCF	−40.424498	1.0859	3076 (0)	1599 (0)	3193 (67.3)	1377 (29.7)
6-311G(d,p) MP2	−40.379223	1.0902	3076 (0)	1580 (0)	3213 (65.1)	1364 (41.9)
6-311++G(d,p) MP2	−40.379638	1.0903	3073 (0)	1571 (0)	3210 (61.6)	1363 (43.6)
6-311G(3d,3p) MP2	−40.394501	1.0857	3060 (0)	1597 (0)	3192 (55.0)	1366 (29.2)
6-311++G(3d,3p) MP2	−40.394792	1.0858	3058 (0)	1597 (0)	3191 (54.4)	1365 (30.8)
cc-pVTZ MP2	−40.411666	1.0853	3077 (0)	1586 (0)	3213 (49.8)	1350 (35.9)
aug-cc-pVTZ MP2	−40.414459	1.0861	3069 (0)	1589 (0)	3205 (48.8)	1356 (32.7)
cc-pVQZ MP2	−40.426306	1.0840	3078 (0)	1585 (0)	3216 (46.6)	1351 (35.8)
DZP CISD	−40.382692	1.0929	3101 (0)	1589 (0)	3238 (89.7)	1381 (41.4)
TZ2P CISD	−40.406100	1.0840	3081 (0)	1605 (0)	3191 (76.8)	1385 (29.4)
TZ3P CISD	−40.407841	1.0859	3061 (0)	1609 (0)	3174 (76.1)	1388 (25.6)
TZ2P(f,d) CISD	−40.421843	1.0844	3085 (0)	1596 (0)	3204 (69.8)	1376 (32.2)
TZ2P(f,d)+diff CISD	−40.421900	1.0844	3084 (0)	1594 (0)	3203 (69.9)	1375 (32.2)
TZ3P(2f,2d) CISD	−40.425430	1.0839	3083 (0)	1600 (0)	3200 (68.1)	1379 (29.4)
TZ3P(2f,2d)+2diff CISD	−40.425513	1.0839	3082 (0)	1600 (0)	3199 (63.2)	1379 (29.6)
6-311G(d,p) CISD	−40.393003	1.0907	3077 (0)	1588 (0)	3195 (85.6)	1380 (34.9)
6-311++G(d,p) CISD	−40.393409	1.0908	3075 (0)	1580 (0)	3193 (82.4)	1379 (35.9)
6-311G(3d,3p) CISD	−40.406340	1.0862	3062 (0)	1605 (0)	3175 (74.4)	1385 (25.9)
6-311++G(3d,3p) CISD	−40.406607	1.0862	3061 (0)	1605 (0)	3174 (74.0)	1384 (27.0)
cc-pVDZ CISD	−40.375626	1.1001	3083 (0)	1571 (0)	3214 (70.3)	1354 (28.5)
aug-cc-pVDZ CISD	−40.382538	1.0986	3064 (0)	1559 (0)	3188 (78.5)	1343 (23.9)
cc-pVTZ CISD	−40.422120	1.0852	3081 (0)	1596 (0)	3198 (69.2)	1370 (31.8)
aug-cc-pVTZ CISD	−40.424498	1.0859	3076 (0)	1599 (0)	3193 (67.3)	1377 (29.7)
6-311G(d,p) CCD	−40.400663	1.0926	3056 (0)	1576 (0)	3181 (80.0)	1370 (34.7)
6-311++G(d,p) CCD	−40.401043	1.0927	3054 (0)	1567 (0)	3178 (76.8)	1369 (35.8)
6-311G(3d.3p) CCD	−40.414453	1.0882	3037 (0)	1594 (0)	3155 (70.1)	1374 (25.5)
6-311++G(3d,3p) CCD	−40.414733	1.0883	3037 (0)	1594 (0)	3154 (69.5)	1373 (26.7)
cc-pVTZ CCD	−40.430991	1.0873	3056 (0)	1583 (0)	3177 (64.1)	1357 (32.0)
aug-cc-pVTZ CCD	−40.433543	1.0881	3050 (0)	1586 (0)	3171 (62.2)	1364 (29.9)
6-311G(d,p) QCISD	−40.401643	1.0932	3047 (0)	1573 (0)	3167 (85.6)	1367 (33.3)
6-311++G(d,p) QCISD	−40.402137	1.0934	3044 (0)	1564 (0)	3163 (82.5)	1366 (34.4)
6-311G(3d,3p) QCISD	−40.415614	1.0888	3029 (0)	1591 (0)	3143 (74.8)	1371 (24.2)
6-311++G(3d,3p) QCISD	−40.415900	1.0889	3028 (0)	1591 (0)	3142 (74.4)	1370 (25.4)
cc-pVTZ QCISD	−40.433209	1.0879	3048 (0)	1581 (0)	3165 (69.6)	1356 (30.5)
aug-cc-pVTZ QCISD	−40.434640	1.0887	3042 (0)	1584 (0)	3159 (67.8)	1363 (28.3)
DZP CCSD	−40.390651	1.0952	3074 (0)	1575 (0)	3213 (87.9)	1369 (40.3)
TZ2P CCSD	−40.414935	1.0863	3051 (0)	1591 (0)	3161 (76.0)	1371 (28.4)
TZ3P CCSD	−40.416839	1.0883	3032 (0)	1596 (0)	3145 (75.4)	1375 (24.4)
TZ2P(f,d) CCSD	−40.431482	1.0868	3055 (0)	1581 (0)	3175 (69.0)	1362 (31.2)
TZ2P(f,d)+diff CCSD	−40.431541	1.0868	3054 (0)	1579 (0)	3173 (69.1)	1361 (31.2)
TZ3P(2f,2d) CCSD	−40.435231	1.0863	3053 (0)	1586 (0)	3170 (67.3)	1365 (28.4)
TZ3P(2f,2d)+2diff CCSD	−40.435320	1.0864	3052 (0)	1585 (0)	3169 (67.4)	1365 (28.6)
cc-pVDZ CCSD	−40.383849	1.1026	3054 (0)	1558 (0)	3187 (69.7)	1342 (27.2)
aug-cc-pVDZ CCSD	−40.391245	1.1013	3033 (0)	1544 (0)	3159 (77.6)	1330 (22.8)
cc-pVTZ CCSD	−40.431822	1.0877	3051 (0)	1581 (0)	3168 (68.3)	1356 (30.9)
aug-cc-pVTZ CCSD	−40.434375	1.0885	3045 (0)	1584 (0)	3162 (66.5)	1363 (28.7)
DZP CCSD(T)	−40.394172	1.0961	3062 (0)	1567 (0)	3202 (88.1)	1361 (40.4)
TZ2P CCSD(T)	−40.420369	1.0876	3034 (0)	1581 (0)	3146 (75.3)	1360 (28.1)
TZ3P CCSD(T)	−40.422442	1.0898	3013 (0)	1586 (0)	3129 (74.8)	1364 (23.9)
TZ2P(f,d) CCSD(T)	−40.437657	1.0880	3039 (0)	1570 (0)	3161 (67.6)	1349 (31.1)
TZ2P(f,d)+diff CCSD(T)	−40.437720	1.0880	3038 (0)	1568 (0)	3159 (67.7)	1349 (31.1)
TZ3P(2f,2d) CCSD(T)	−40.441766	1.0877	3036 (0)	1575 (0)	3155 (65.9)	1352 (28.1)
TZ3P(2f,2d)+2diff CCSD(T)	−40.441860	1.0877	3035 (0)	1575 (0)	3154 (66.0)	1352 (28.3)
cc-pVDZ CCSD(T)	−40.387627	1.1037	3040 (0)	1551 (0)	3175 (71.5)	1334 (26.5)
aug-cc-pVDZ CCSD(T)	−40.395820	1.1026	3016 (0)	1535 (0)	3144 (78.4)	1320 (22.2)
cc-pVTZ CCSD(T)	−40.438099	1.0890	3035 (0)	1571 (0)	3154 (66.8)	1344 (30.9)
aug-cc-pVTZ CCSD(T)	−40.440930	1.0899	3028 (0)	1574 (0)	3147 (65.1)	1351 (28.4)
expt.[a]		1.0858	3026	1583	3157	1367
expt [b]		1.0862				
expt.[c]		1.0870				
expt.[d]					(69 ± 3)	(29 ± 1)
expt.[e]					(72 ± 11)	(41 ± 6)
expt.[f]					(70 ± 3)	

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TABLE 3: Theoretical Predictions of the Total Energy (in hartree), Geometrical Parameters (bond lengths in Å, angle in degree), Dipole Moment (in debye), HarmonicVibrational Frequencies (in Cm^{-1}), and Infrared Intensities (in parenthesis in Km mol^{-1}) for the H_2CO Molecule

level of theory	energy	r_e(CO)	r_e(CH)	α_e	μ_e	$\omega_{1,a_1}(I_1)$	$\omega_{2,a_1}(I_2)$	$\omega_{3,a_1}(I_3)$	$\omega_{4,b_1}(I_4)$	$\omega_{5,b_2}(I_5)$	$\omega_{6,b_2}(I_6)$
DZ SCF	−113.830712	1.2170	1.0843	116.87	3.1904	3224 (55.7)	1878 (100.4)	1651 (29.2)	1325 (9.0)	3315 (96.5)	1350 (15.1)
TZ SCF	−113.848250	1.2082	1.0821	117.02	3.0775	3131 (24.4)	1874 (97.5)	1663 (31.5)	1335 (3.9)	3221 (76.3)	1379 (18.3)
DZP SCF	−113.894229	1.1884	1.0959	116.19	2.7775	3136 (72.4)	2008 (158.5)	1653 (14.8)	1333 (2.0)	3214 (111.6)	1366 (19.0)
TZ2P SCF	−113.913442	1.1780	1.0911	116.14	2.6947	3101 (64.4)	1986 (156.0)	1653 (19.0)	1341 (2.2)	3175 (109.7)	1373 (22.3)
TZ3P SCF	−113.914372	1.1790	1.0922	116.19	2.6877	3087 (64.6)	1991 (154.3)	1651 (20.0)	1336 (3.7)	3158 (100.1)	1369 (21.3)
TZ2P(f,d) SCF	−113.917402	1.1772	1.0924	115.98	2.6893	3090 (65.9)	1995 (160.5)	1651 (17.4)	1341 (2.0)	3161 (112.3)	1369 (22.6)
TZ2P(f,d)+diff SCF	−113.917740	1.1774	1.0925	116.03	2.7202	3089 (64.7)	1993 (162.8)	1649 (17.7)	1340 (2.3)	3159 (100.6)	1367 (20.3)
TZ3P(2f,2d) SCF	−113.918236	1.1772	1.0925	116.06	2.6799	3086 (65.8)	1993 (156.1)	1650 (19.5)	1338 (3.5)	3156 (101.0)	1371 (21.5)
TZ3P(2f,2d)+2diff SCF	−113.918557	1.1774	1.0925	116.11	2.7096	3086 (66.4)	1191 (159.9)	1649 (19.4)	1337 (3.8)	3156 (96.2)	1369 (20.9)
6-311G(d,p) SCF	−113.906284	1.1766	1.0927	116.05	2.5850	3081 (63.4)	1999 (140.7)	1648 (19.3)	1337 (4.0)	3147 (102.9)	1364 (22.7)
6-311++G(d,p) SCF	−113.902874	1.1797	1.0943	116.05	2.8054	3097 (61.0)	1996 (173.9)	1650 (15.4)	1337 (1.8)	3169 (110.5)	1363 (19.3)
6-311G(3d,3p) SCF	−113.906284	1.1766	1.0927	116.05	2.5851	3081 (63.4)	1999 (140.7)	1649 (19.3)	1337 (4.0)	3147 (102.9)	1364 (22.7)
6-311++(3d,3p) SCF	−113.909221	1.1780	1.0923	116.21	2.7296	3087 (66.4)	1990 (159.9)	1646 (19.9)	1333 (4.0)	3157 (95.0)	1365 (20.7)
cc-pVDZ SCF	−113.877223	1.1821	1.1018	115.63	2.5684	3109 (50.8)	2013 (158.9)	1637 (11.1)	1325 (1.0)	3183 (134.5)	1360 (26.2)
aug-cc-pVDZ SCF	−113.886021	1.1849	1.0993	116.32	2.7492	3106 (64.3)	1979 (155.7)	1630 (20.6)	1326 (4.2)	3184 (93.8)	1348 (20.5)
cc-pVTZ SCF	−113.913226	1.1779	1.0929	115.94	2.6538	3084 (62.6)	1999 (152.3)	1652 (16.7)	1337 (2.2)	3153 (115.3)	1370 (22.1)
aug-cc-pVTZ SCF	−113.915337	1.1785	1.0927	116.11	2.7162	3087 (65.9)	1992 (160.1)	1648 (19.5)	1335 (4.0)	3155 (96.0)	1367 (20.7)
cc-pVQZ SCF	−113.922383	1.1764	1.0925	116.01	2.6820	3085 (64.9)	1997 (157.4)	1652 (18.3)	1338 (2.7)	3153 (104.7)	1372 (21.7)
aug-cc-pVQZ SCF	−113.922938	1.1767	1.0925	116.07	2.7029	3085 (66.8)	1994 (160.9)	1651 (19.5)	1337 (3.9)	3154 (97.7)	1371 (21.0)
cc-pV5Z SCF	−113.924607	1.1764	1.0924	116.06	2.6985	3086 (66.2)	1995 (160.6)	1651 (19.1)	1338 (3.3)	3155 (100.1)	1372 (21.3)
aug-cc-pV5Z SCF	−113.924692	1.1764	1.0924	116.07	2.7017	3086 (66.8)	1994 (160.9)	1651 (19.5)	1337 (3.8)	3155 (97.8)	1371 (21.1)
6-311G(d,p) MP2	−114.235171	1.2106	1.1061	115.73	2.8110	2964 (61.1)	1777 (64.7)	1567 (5.1)	1211 (2.7)	3030 (146.1)	1291 (14.3)
6-311++G(d,p) MP2	−114.241772	1.2130	1.1048	116.14	2.9817	2975 (66.4)	1762 (73.6)	1559 (6.6)	1207 (5.1)	3047 (116.3)	1278 (8.4)
6-311G(3d,3p) MP2	−114.269258	1.2098	1.1004	116.23	2.7478	2954 (67.2)	1759 (55.1)	1549 (9.8)	1205 (6.3)	3023 (105.7)	1272 (12.6)
6-311++G(3d,3p) MP2	−114.274112	1.2122	1.0998	116.51	2.9078	2962 (70.6)	1748 (68.5)	1545 (10.9)	1198 (6.6)	3036 (94.6)	1274 (10.1)
cc-pVTZ MP2	−114.307198	1.2105	1.1005	116.17	2.8177	2970 (63.7)	1772 (61.8)	1553 (8.4)	1209 (4.2)	3043 (113.9)	1280 (10.8)
aug-cc-pVTZ MP2	−114.316410	1.2129	1.1002	116.59	2.8944	2973 (66.7)	1753 (67.8)	1540 (10.7)	1198 (7.0)	3048 (88.4)	1267 (9.4)
cc-pVQZ MP2	−114.344707	1.2082	1.0992	116.44	2.8450	2975 (65.2)	1769 (66.6)	1548 (9.7)	1206 (4.8)	3051 (97.8)	1278 (10.2)
aug-cc-pVQZ MP2	−114.348667	1.2094	1.0993	116.63	2.8726						
DZP CISD	−114.192792	1.2116	1.1042	116.21	2.4952	3053 (65.9)	1867 (95.2)	1585 (7.4)	1233 (3.6)	3132 (112.9)	1299 (13.2)
TZ2P CISD	−114.254238	1.1971	1.0942	116.33	2.4461	3020 (60.9)	1857 (98.8)	1590 (12.6)	1247 (3.6)	3095 (108.6)	1318 (15.5)
TZ3P CISD	−114.259565	1.1984	1.0957	116.32	2.4413	3009 (60.1)	1863 (96.6)	1594 (13.3)	1244 (5.3)	3081 (97.4)	1316 (14.8)
TZ2P(f,d) CISD	−114.286824	1.1948	1.0950	116.20	2.4595	3028 (58.8)	1877 (103.5)	1587 (11.1)	1253 (3.5)	3102 (104.1)	1311 (15.4)
TZ2P(f,d)+diff CISD	−114.287497	1.1950	1.0951	116.27	2.4938	3026 (57.8)	1875 (105.1)	1585 (11.2)	1251 (4.0)	3097 (91.6)	1308 (13.2)
TZ3P(2f,2d) CISD	−114.296292	1.1946	1.0947	116.36	2.4627	3021 (58.5)	1873 (99.3)	1585 (13.7)	1246 (5.1)	3094 (91.1)	1314 (14.5)
TZ3P(2f,2d)+2diff CISD	−114.296900	1.1948	1.0947	116.44	2.4972	3021 (59.3)	1871 (102.4)	1583 (13.6)	1243 (5.5)	3093 (85.8)	1311 (13.8)
6-311G(d,p) CISD	−114.222471	1.1974	1.1025	115.74	2.3155	3007 (52.3)	1879 (98.5)	1595 (6.9)	1243 (2.0)	3071 (134.0)	1316 (6.9)
6-311++G(d,p) CISD	−114.227877	1.1988	1.1017	116.08	2.5004	3015 (57.3)	1869 (109.6)	1306 (12.9)	1241 (3.6)	3083 (110.3)	1306 (12.9)
6-311G(3d,3p) CISD	−114.251644	1.1950	1.0971	116.12	2.3211	2996 (59.2)	1870 (88.0)	1584 (11.9)	1245 (5.4)	3061 (100.6)	1305 (16.7)
6-311++G(3d,3p) CISD	−114.255654	1.1966	1.0966	116.33	2.4880	3002 (62.1)	1863 (103.3)	1581 (12.3)	1239 (5.4)	3072 (91.8)	1307 (14.4)
cc-pVDZ CISD	−114.184376	1.2030	1.1129	115.31	2.2252	3007 (50.5)	1881 (99.8)	1574 (5.1)	1229 (2.0)	3073 (147.0)	1300 (19.3)
aug-cc-pVDZ CISD	−114.206252	1.2078	1.1084	116.49	2.5037	3016 (59.9)	1841 (98.6)	1560 (12.6)	1226 (5.8)	3094 (92.2)	1283 (14.0)
cc-pVTZ CISD	−114.286938	1.1952	1.0964	116.11	2.4047	3018 (55.4)	1885 (96.4)	1590 (10.8)	1252 (3.6)	3087 (106.1)	1314 (15.1)
aug-cc-pVTZ CISD	−114.294321	1.1964	1.0962	116.39	2.5032	3021 (58.1)	1875 (103.3)	1580 (12.8)	1245 (5.9)	3090 (85.2)	1305 (13.8)
6-311G(d,p) CCD	−114.243808	1.2014	1.1065	115.81	2.2253	2961 (49.9)	1852 (77.1)	1577 (4.8)	1215 (2.7)	3028 (131.0)	1300 (18.3)
6-311++G(d,p) CCD	−114.249506	1.2028	1.1058	116.13	2.4186	2969 (54.9)	1843 (87.8)	1569 (5.8)	1212 (4.6)	3039 (107.6)	1290 (12.4)
6-311G(3d,3p) CCD	−114.277539	1.1997	1.1012	116.24	2.2464	2946 (57.0)	1838 (70.5)	1562 (9.4)	1214 (6.3)	3014 (98.8)	1287 (16.1)
6-311++G(3d,3p) CCD	−114.279612	1.2015	1.1007	116.46	2.4203	2952 (59.7)	1831 (84.8)	1558 (9.8)	1208 (6.5)	3024 (89.8)	1289 (13.7)
cc-pVTZ CCD	−114.313468	1.2001	1.1007	116.22	2.3291	2965 (52.9)	1853 (77.6)	1566 (8.6)	1221 (4.5)	3038 (103.6)	1296 (14.3)
aug-cc-pVTZ CCD	−114.321704	1.2016	1.1006	116.52	2.4369	2967 (55.4)	1840 (84.4)	1554 (10.5)	1212 (7.0)	3040 (82.7)	1284 (12.8)
6-311G(d,p) QCISD	−114.249549	1.2065	1.1078	115.66	2.2355	2945 (57.9)	1913 (84.9)	1566 (7.1)	1207 (2.0)	3003 (146.0)	1290 (16.6)
6-311++G(d,p) QCISD	−114.255567	1.2081	1.1068	116.03	2.4370	2954 (63.4)	1800 (95.4)	1558 (8.3)	1204 (3.8)	3017 (119.0)	1280 (10.6)
6-311G(3d,3p) QCISD	−114.281086	1.2043	1.1023	116.13	2.2466	2931 (63.9)	1801 (73.8)	1551 (11.5)	1206 (5.5)	2992 (108.8)	1277 (14.6)
6-311++G(3d,3p) QCISD	−114.285472	1.2063	1.1017	116.37	2.4278	2938 (67.0)	1792 (88.3)	1547 (12.2)	1199 (5.6)	3004 (98.7)	1279 (12.1)
cc-pVTZ QCISD	−114.318766	1.2046	1.1017	116.11	2.3302	2952 (59.0)	1817 (81.2)	1557 (10.6)	1213 (3.8)	3017 (114.1)	1287 (12.8)
aug-cc-pVTZ QCISD	−114.326981	1.2061	1.1014	116.44	2.4420	2955 (61.6)	1803 (87.4)	1545 (12.5)	1204 (6.2)	3021 (90.6)	1275 (11.4)
DZP CCSD	−114.217002	1.2196	1.1083	116.27	2.4260	3004 (65.8)	1813 (77.3)	1560 (6.6)	1199 (4.1)	3083 (113.4)	1278 (11.8)
TZ2P CCSD	−114.281922	1.2050	1.0984	116.42	2.3795	2962 (61.5)	1800 (81.9)	1561 (11.9)	1211 (4.1)	3036 (111.2)	1295 (13.9)
TZ3P CCSD	−114.287674	1.2064	1.1000	116.40	2.3734	2952 (60.7)	1807 (79.7)	1566 (12.3)	1207 (5.9)	3024 (99.7)	1292 (13.2)
TZ2P(f,d) CCSD	−114.317021	1.2027	1.0994	116.30	2.3926	2970 (58.8)	1820 (86.0)	1557 (10.2)	1216 (4.1)	3043 (106.2)	1287 (13.7)
TZ2P(f,d)+diff CCSD	−114.317773	1.2030	1.0996	116.38	2.4301	2968 (58.0)	1817 (87.7)	1555 (10.3)	1213 (4.7)	3038 (93.0)	1283 (11.5)
TZ3P(2f,2d) CCSD	−114.327182	1.2027	1.0993	116.47	2.3957	2962 (58.7)	1815 (81.6)	1555 (12.8)	1208 (5.8)	3033 (92.6)	1289 (12.8)
TZ3P(2f,2d)+2diff CCSD	−114.327849	1.2030	1.0992	116.56	2.4338	2962 (59.3)	1812 (84.8)	1552 (12.6)	1205 (6.2)	3033 (86.8)	1286 (12.1)
cc-pVDZ CCSD	−114.208911	1.2103	1.1178	115.28	2.1386	2952 (53.1)	1829 (83.9)	1549 (4.4)	1195 (2.2)	3016 (152.0)	1279 (17.7)
aug-cc-pVDZ CCSD	−114.232910	1.2161	1.1132	116.59	2.4390	2959 (61.1)	1784 (81.7)	1532 (11.6)	1189 (6.3)	3037 (93.6)	1260 (12.3)
cc-pVTZ CCSD	−114.317299	1.2030	1.1011	116.17	2.3297	2958 (55.7)	1830 (79.6)	1561 (9.8)	1215 (4.1)	3026 (108.4)	1290 (13.4)
aug-cc-pVTZ CCSD	−114.325464	1.2045	1.1009	116.50	2.4390	2961 (58.1)	1817 (85.7)	1549 (11.7)	1206 (6.6)	3030 (86.3)	1279 (12.0)
DZP CCSD(T)	−114.226409	1.2246	1.1101	116.26	2.3847	2979 (67.7)	1774 (69.9)	1545 (7.0)	1180 (4.4)	3058 (119.4)	1265 (10.6)
TZ2P CCSD(T)	−114.296729	1.2118	1.1005	116.47	2.3341	2933 (64.4)	1752 (71.4)	1542 (12.9)	1187 (4.3)	3007 (118.5)	1279 (12.4)
TZ3P CCSD(T)	−114.302972	1.2133	1.1022	116.45	2.3271	2923 (63.7)	1758 (69.3)	1547 (13.2)	1183 (6.1)	2994 (106.5)	1276 (11.7)
TZ2P(f,d) CCSD(T)	−114.333199	1.2094	1.1014	116.36	2.3441	2943 (61.3)	1770 (75.4)	1539 (10.4)	1192 (4.3)	3014 (112.9)	1271 (12.3)
TZ2P(f,d)+diff CCSD(T)	−114.334029	1.2098	1.1015	116.44	2.3838	2940 (60.5)	1767 (77.1)	1537 (10.5)	1189 (5.0)	3009 (98.7)	1266 (10.1)
TZ3P(2f,2d) CCSD(T)	−114.344353	1.2097	1.1013	116.53	2.3476	2933 (61.1)	1764 (70.6)	1536 (13.2)	1184 (6.0)	3004 (98.4)	1272 (11.3)
TZ3P(2f,2d)+2diff CCSD(T)	−114.345075	1.2100	1.1013	116.63	2.3886	2933 (61.9)	1761 (73.8)	1533 (13.0)	1180 (6.5)	3004 (92.1)	1269 (10.6)
cc-pVDZ CCSD(T)	−114.219034	1.2156	1.1199	115.21	2.0860	2925 (56.8)	1787 (77.1)	1535 (4.6)	1176 (2.3)	2986 (164.1)	1266 (16.1)
aug-cc-pVDZ CCSD(T)	−114.245210	1.2226	1.1153	116.65	2.3989	2932 (64.3)	1737 (72.2)	1515 (12.1)	1167 (6.5)	3009 (100.4)	1245 (11.1)
cc-pVTZ CCSD(T)	−114.333872	1.2096	1.1033	116.19	2.2725	2929 (58.4)	1781 (69.3)	1543 (9.9)	1192 (4.3)	2996 (115.7)	1275 (11.9)
aug-cc-pVTZ CCSD(T)	−114.342934	1.2115	1.1031	116.57	2.3935	2932 (60.7)	1765 (74.9)	1530 (11.8)	1181 (6.9)	3000 (91.5)	1262 (10.6)
expt.[a]		1.203	1.099	116.5							
expt.[b]		1.2033	1.1005	116.18							
expt.[c]					2.323						
expt.[d]					2.331						
expt.[e]						2944	1764	1563	1191	3009	1288
expt.[f]						2944	1761	1517	1187	3033	1282
expt.[g,h]						2978	1778	1529	1191	2997	1299
expt.[i]						(75.5)	(74.0)	(11.2)	(6.5)	(87.6)	(9.9)

[a] Yamada, K.; Nakagawa, T.; Kuchitsu, K.; Morino, Y. *J. Mol. Spectrosc.* **1971**, *38*, 70. [b] Duncan, J. L. *Mol. Phys.* **1974**, *28*, 1177. [c] Kondo, K.; Oka, T. *J. Phys. Soc. Jpn.* **1960**, *15*, 307. [d] Fabricant, B.; Krieger, D.; Muenter, J. S. *J. Chem. Phys.* **1977**, *67*, 1576. [e] Duncan, J. L.; Mallinson, P. D. *Chem. Phys. Lett.* **1973**, *23*, 597. [f] Tanaka, Y.; Machida, K. *J. Mol. Spectrosc.* **1977**, *64*, 429. [g] Reisner, D. E.; Field, R. W.; Kinsey, J. L.; Dai, H. L. *J. Chem. Phys.* **1984**, *80*, 5968. [h] Wohar, M. W.; Jadgodzinski, P. W. *J. Mol. Spectrosc.* **1991**, *148*, 13. [i] Nakanaga, T.; Kondo, S.; Saeki, S. *J. Chem. Phys.* **1982**, *76*, 3860. Intensities include overlapped combination bands.

TABLE 4: Theoretical Predictions of the Total Energy (in hartree), Geometrical Parameters (bond lengths in Å), Harmonic Vibrational Frequencies (in Cm^{-1}), and Infrared Intensities (in parenthesis in Km mol^{-1}) for the C_2H_2 Molecule

level of theory	energy	r_e(CC)	r_e(CH)	$\omega_{1,\sigma_g}(I_1)$	$\omega_{2,\sigma_g}(I_2)$	$\omega_{3,\sigma_u}(I_3)$	$\omega_{4,\pi_g}(I_4)$	$\omega_{5,\pi_u}(I_5)$
DZ SCF	−76.799232	1.2010	1.0538	3732 (0)	2168 (0)	3622 (87.8)	843 (0)	887 (313.1)
TZ SCF	−76.815783	1.1883	1.0526	3656 (0)	2181 (0)	3532 (98.1)	919 (0)	887 (343.8)
DZP SCF	−76.831521	1.1914	1.0615	3674 (0)	2204 (0)	3570 (100.9)	767 (0)	857 (228.8)
TZ2P SCF	−76.849070	1.1801	1.0539	3669 (0)	2209 (0)	3558 (96.7)	786 (0)	858 (236.8)
TZ3P SCF	−76.849773	1.1807	1.0545	3663 (0)	2214 (0)	3552 (96.6)	790 (0)	859 (223.3)
TZ2P(f,d) SCF	−76.852431	1.1802	1.0542	3672 (0)	2213 (0)	3562 (95.0)	816 (0)	872 (231.2)
TZ2P(f,d)+diff SCF	−76.852472	1.1803	1.0542	3672 (0)	2212 (0)	3561 (95.8)	816 (0)	871 (239.8)
TZ3P(2f,2d) SCF	−76.852919	1.1797	1.0540	3667 (0)	2211 (0)	3549 (94.5)	813 (0)	869 (218.6)
TZ3P(2f,2d)+2diff SCF	−76.852988	1.1797	1.0540	3667 (0)	2210 (0)	3548 (95.1)	813 (0)	869 (225.4)
6-311G(d,p) SCF	−76.841238	1.1823	1.0555	3676 (0)	2215 (0)	3562 (95.6)	815 (0)	875 (217.1)
6-311++G(d,p) SCF	−76.842778	1.1835	1.0558	3675 (0)	2206 (0)	3561 (101.3)	817 (0)	872 (252.6)
6-311G(3d,3p) SCF	−76.845099	1.1792	1.0539	3665 (0)	2213 (0)	3553 (89.7)	807 (0)	870 (200.8)
6-311++G(3d,3p) SCF	−76.846452	1.1806	1.0539	3664 (0)	2203 (0)	3552 (96.8)	799 (0)	865 (225.1)
cc-pVDZ SCF	−76.826043	1.1918	1.0639	3689 (0)	2224 (0)	3577 (104.2)	784 (0)	866 (190.3)
aug-cc-pVDZ SCF	−76.828728	1.1921	1.0626	3677 (0)	2209 (0)	3564 (100.6)	736 (0)	840 (231.1)
cc-pVTZ SCF	−76.850624	1.1801	1.0539	3674 (0)	2213 (0)	3556 (94.8)	807 (0)	868 (220.9)
aug-cc-pVTZ SCF	−76.851376	1.1803	1.0539	3674 (0)	2210 (0)	3554 (95.6)	810 (0)	869 (226.0)
cc-pVQZ SCF	−76.855726	1.1792	1.0539	3665 (0)	2211 (0)	3555 (93.9)	810 (0)	867 (224.8)
aug-cc-pVQZ SCF	−76.855875	1.1793	1.0539	3665 (0)	2210 (0)	3555 (94.2)	811 (0)	966 (224.7)
cc-pV5Z SCF	−76.856845	1.1792	1.0539	3665 (0)	2211 (0)	3555 (94.1)	813 (0)	967 (226.9)
6-311G(d,p) MP2	−77.111243	1.2150	1.0646	3550 (0)	1970 (0)	3460 (92.4)	562 (0)	770 (178.9)
6-311++G(d,p) MP2	−77.113302	1.2163	1.0648	3549 (0)	1963 (0)	3459 (95.5)	526 (0)	764 (209.6)
6-311G(3d,3p) MP2	−77.131876	1.2111	1.0609	3525 (0)	1959 (0)	3436 (86.5)	528 (0)	765 (163.9)
6-311++G(3d,3p) MP2	−77.133537	1.2123	1.0613	3520 (0)	1953 (0)	3431 (91.4)	480 (0)	740 (183.7)
cc-pVTZ MP2	−77.159196	1.2112	1.0615	3542 (0)	1976 (0)	3447 (96.0)	589 (0)	753 (178.8)
aug-cc-pVTZ MP2	−77.164058	1.2122	1.0617	3534 (0)	1968 (0)	3432 (95.6)	601 (0)	754 (179.5)
cc-pVQZ MP2	−77.183473	1.2086	1.0611	3531 (0)	1978 (0)	3444 (96.0)	600 (0)	752 (179.6)
DZP CISD	−77.080812	1.2138	1.0691	3574 (0)	2072 (0)	3480 (83.6)	621 (0)	762 (190.0)
TZ2P CISD	−77.123461	1.1959	1.0585	3566 (0)	2089 (0)	3461 (83.3)	617 (0)	777 (200.1)
TZ3P CISD	−77.125986	1.1977	1.0593	3562 (0)	2093 (0)	3458 (84.4)	625 (0)	780 (190.0)
TZ2P(f,d) CISD	−77.147343	1.1952	1.0577	3591 (0)	2105 (0)	3490 (88.3)	670 (0)	805 (194.4)
TZ2P(f,d)+diff CISD	−77.147549	1.1953	1.0578	3591 (0)	2104 (0)	3489 (88.8)	675 (0)	803 (202.4)
TZ3P(2f,2d) CISD	−77.152272	1.1941	1.0577	3574 (0)	2100 (0)	3458 (87.6)	653 (0)	790 (185.5)
TZ3P(2f,2d)+2diff CISD	−77.152481	1.1941	1.0577	3574 (0)	2100 (0)	3457 (87.9)	641 (0)	791 (190.0)
6-311G(d,p) CISD	−77.104878	1.2012	1.0623	3587 (0)	2088 (0)	3484 (86.2)	642 (0)	804 (184.4)
6-311++G(d,p) CISD	−77.106591	1.2022	1.0626	3585 (0)	2082 (0)	3482 (90.0)	614 (0)	801 (214.1)
6-311G(3d,3p) CISD	−77.122019	1.1963	1.0586	3564 (0)	2085 (0)	3461 (79.9)	583 (0)	788 (172.2)
6-311++G(3d,3p) CISD	−77.123398	1.1975	1.0588	3561 (0)	2077 (0)	3458 (84.9)	574 (0)	781 (191.1)
cc-pVDZ CISD	−77.078424	1.2150	1.0737	3573 (0)	2087 (0)	3474 (92.3)	631 (0)	784 (161.8)
aug-cc-pVDZ CISD	−77.086839	1.2157	1.0727	3557 (0)	2074 (0)	3456 (87.1)	505 (0)	744 (195.1)
cc-pVTZ CISD	−77.147229	1.1960	1.0584	3588 (0)	2103 (0)	3479 (90.5)	671 (0)	796 (189.1)
aug-cc-pVTZ CISD	−77.150936	1.1963	1.0585	3583 (0)	2099 (0)	3467 (90.2)	682 (0)	798 (189.9)
6-311G(d,p) CCD	−77.122867	1.2063	1.0656	3547 (0)	2049 (0)	3446 (81.1)	601 (0)	783 (177.9)
6-311++G(d,p) CCD	−77.124641	1.2072	1.0659	3545 (0)	2043 (0)	3443 (84.4)	567 (0)	779 (207.0)
6-311G(3d,3p) CCD	−77.141250	1.2018	1.0622	3517 (0)	2042 (0)	3416 (83.6)	528 (0)	765 (167.3)
6-311++G(3d,3p) CCD	−77.142671	1.2029	1.0624	3514 (0)	2035 (0)	3413 (79.7)	519 (0)	757 (185.5)
cc-pVTZ CCD	−77.168300	1.2012	1.0619	3543 (0)	2064 (0)	3435 (85.8)	634 (0)	773 (182.8)
aug-cc-pVTZ CCD	−77.172489	1.2016	1.0620	3536 (0)	2058 (0)	3420 (85.3)	646 (0)	774 (183.1)
6-311G(d,p) QCISD	−77.126990	1.2096	1.0660	3536 (0)	2023 (0)	3438 (80.1)	577 (0)	774 (175.9)
6-311++G(d,p) QCISD	−77.112876	1.2106	1.0663	3534 (0)	2017 (0)	3436 (83.8)	534 (0)	769 (204.9)
6-311G(3d,3p) QCISD	−77.145263	1.2047	1.0625	3507 (0)	2019 (0)	3410 (73.9)	516 (0)	758 (164.9)
6-311++G(3d,3p) QCISD	−77.146667	1.2059	1.0626	3504 (0)	2012 (0)	3407 (78.7)	507 (0)	750 (183.7)
cc-pVTZ QCISD	−77.172081	1.2042	1.0621	3533 (0)	2040 (0)	3429 (84.8)	617 (0)	766 (181.5)
aug-cc-pVTZ QCISD	−77.177609	1.2045	1.0622	3527 (0)	2035 (0)	3416 (84.4)	630 (0)	768 (182.5)
DZP CCSD	−77.101102	1.2218	1.0726	3525 (0)	2013 (0)	3435 (76.0)	571 (0)	730 (179.7)
TZ2P CCSD	−77.145522	1.2030	1.0620	3512 (0)	2034 (0)	3411 (77.0)	562 (0)	747 (191.9)
TZ3P CCSD	−77.148333	1.2049	1.0629	3510 (0)	2038 (0)	3410 (78.0)	572 (0)	751 (182.6)
TZ2P(f,d) CCSD	−77.171088	1.2022	1.0613	3539 (0)	2051 (0)	3441 (82.4)	621 (0)	777 (186.6)
TZ2P(f,d)+diff CCSD	−77.171315	1.2023	1.0614	3539 (0)	2050 (0)	3441 (82.9)	627 (0)	775 (195.0)
TZ3P(2f,2d) CCSD	−77.176394	1.2012	1.0613	3519 (0)	2046 (0)	3407 (81.7)	602 (0)	761 (178.3)
TZ3P (2f,2d)+2diff CCSD	−77.176619	1.2012	1.0613	3519 (0)	2045 (0)	3407 (82.0)	588 (0)	761 (182.8)
cc-pVDZ CCSD	−77.099264	1.2228	1.0776	3521 (0)	2030 (0)	3426 (85.3)	580 (0)	755 (154.0)
aug-cc-pVDZ CCSD	−77.108528	1.2237	1.0770	3502 (0)	2016 (0)	3405 (80.1)	438 (0)	713 (186.8)
cc-pVTZ CCSD	−77.171184	1.2033	1.0620	3536 (0)	2048 (0)	3430 (84.6)	622 (0)	767 (181.8)
aug-cc-pVTZ CCSD	−77.175230	1.2036	1.0621	3529 (0)	2044 (0)	3417 (84.2)	634 (0)	770 (182.5)
DZP CCSD(T)	−77.111911	1.2272	1.0739	3505 (0)	1974 (0)	3419 (74.7)	530 (0)	708 (177.7)
TZ2P CCSD(T)	−77.160422	1.2093	1.0637	3487 (0)	1986 (0)	3390 (74.8)	512 (0)	726 (187.9)
TZ3P CCSD(T)	−77.163583	1.2114	1.0646	3484 (0)	1991 (0)	3388 (75.5)	523 (0)	730 (179.2)
TZ2P(f,d) CCSD(T)	−77.187284	1.2086	1.0628	3515 (0)	2004 (0)	3421 (80.3)	577 (0)	757 (183.0)
TZ2P(f,d)+diff CCSD(T)	−77.187537	1.2087	1.0630	3515 (0)	2003 (0)	3420 (80.8)	583 (0)	754 (192.2)
TZ3P(2f,2d) CCSD(T)	−77.193246	1.2076	1.0631	3492 (0)	1998 (0)	3385 (79.6)	554 (0)	739 (174.9)
TZ3P(2f,2d)+2diff CCSD(T)	−77.193492	1.2077	1.0631	3492 (0)	1997 (0)	3384 (79.9)	536 (0)	740 (179.6)
cc-pVDZ CCSD(T)	−77.110865	1.2287	1.0790	3500 (0)	1986 (0)	3410 (83.0)	527 (0)	734 (152.1)
aug-cc-pVDZ CCSD(T)	−77.121383	1.2301	1.0787	3479 (0)	1969 (0)	3385 (77.4)	366 (0)	691 (184.8)
cc-pVTZ CCSD(T)	−77.187648	1.2097	1.0637	3511 (0)	2001 (0)	3410 (82.7)	578 (0)	746 (178.8)
aug-cc-pVTZ CCSD(T)	−77.192197	1.2102	1.0640	3503 (0)	1995 (0)	3394 (81.8)	593 (0)	748 (178.9)
expt.[a]		1.20257	1.06215					
expt.[b]				3495	2008	3415	624	747
expt.[c]				(0)	(0)	(71 ± 2)	(0)	(175 ± 5)

[a] Baldachi, A.; Ghersetti, S.; Horlock, S. C.; Rao, K. N. *J. Mol. Spectrosc.* **1976**, *59*, 16. [b] Strey, G.; Mills, I. M. *J. Mol. Spectrosc.* **1976**, *59*, 103. [c] Koops, T.; Smit, W. M. A.; Visser, T. *J. Mol. Struct.* **1984**, *112*, 285.

TABLE 5: Theoretical Predictions of the Total Energy (in hartree), Geometrical Parameters (bond lengths in Å), Dipole Moment (in debye), Harmonic Vibrational Frequencies (in Cm^{-1}), and Infrared Intensities (in parentheses in Km mol^{-1}) for the HCN Molecule

level of theory	energy	r_e(CH)	r_e(CN)	μ_e	$\omega_{1,\sigma^+}(I_1)$	$\omega_{2,\sigma^+}(I_2)$	$\omega_{3,\pi}(I_3)$
DZ SCF	−92.836938	1.0542	1.1507	3.2963	3697 (66.7)	2327 (12.8)	883 (131.3)
TZ SCF	−92.855738	1.0533	1.1367	3.2846	3602 (78.1)	2324 (10.7)	867 (145.4)
DZP SCF	−92.889164	1.0638	1.1366	3.2143	3629 (69.0)	2403 (12.9)	856 (84.5)
TZ2P SCF	−92.909284	1.0569	1.1239	3.2597	3612 (74.0)	2405 (9.8)	865 (73.8)
TZ3P SCF	−92.910035	1.0574	1.1250	3.2564	3607 (71.3)	2407 (9.6)	865 (69.6)
TZ2P(f,d) SCF	−92.912675	1.0569	1.1242	3.2570	3619 (72.6)	2410 (10.3)	883 (70.8)
TZ2P(f,d)+diff SCF	−92.912907	1.0571	1.1241	3.2652	3616 (71.5)	2410 (10.7)	883 (74.6)
TZ3P(2f,2d) SCF	−92.913211	1.0565	1.1238	3.2503	3610 (69.9)	2407 (10.2)	879 (68.6)
TZ3P(2f,2d)+2diff SCF	−92.913394	1.0566	1.1239	3.2638	3609 (70.3)	2406 (11.0)	879 (69.2)
6-311G(d,p) SCF	−92.899548	1.0578	1.1265	3.2052	3624 (70.0)	2413 (10.4)	892 (73.6)
6-311++G(d,p) SCF	−92.901470	1.0581	1.1271	3.2742	3622 (72.0)	2406 (12.2)	877 (79.4)
6-311G(3d,3p) SCF	−92.904489	1.0563	1.1239	3.1891	3612 (68.3)	2408 (9.4)	865 (63.1)
6-311++G(3d,3p) SCF	−92.906376	1.0567	1.1246	3.2703	3609 (71.0)	2400 (11.0)	870 (34.4)
cc-pVDZ SCF	−92.884217	1.0667	1.1343	3.1296	3645 (75.5)	2421 (12.3)	869 (71.7)
aug-cc-pVDZ SCF	−92.888433	1.0650	1.1342	3.2828	3621 (72.6)	2401 (11.4)	852 (72.0)
cc-pVTZ SCF	−92.910230	1.0565	1.1247	3.2268	3619 (66.7)	2407 (9.8)	876 (71.1)
aug-cc-pVTZ SCF	−92.911314	1.0568	1.1244	3.2630	3615 (70.4)	2405 (11.0)	878 (71.2)
cc-pVQZ SCF	−92.916736	1.0570	1.1233	3.2517	3607 (70.4)	2408 (10.2)	877 (69.9)
cc-pV5Z SCF	−92.918058	1.0569	1.1232	3.2609	3609 (70.1)	2408 (10.7)	877 (69.5)
6-311G(d,p) MP2	−93.200207	1.0673	1.1706	3.2444	3490 (72.5)	2022 (0.5)	758 (73.1)
6-311++G(d,p) MP2	−93.203224	1.0682	1.1713	3.3194	3481 (77.0)	2016 (0.3)	730 (86.3)
6-311G(3d,3p) MP2	−93.223594	1.0641	1.1666	3.2226	3461 (71.2)	2015 (0.5)	707 (65.8)
6-311++G(3d,3p) MP2	−93.226656	1.0648	1.1671	3.3087	3454 (75.5)	2012 (0.3)	711 (73.2)
cc-pVTZ MP2	−93.253589	1.0643	1.1668	3.2613	3476 (71.7)	2027 (0.4)	719 (72.6)
aug-cc-pVTZ MP2	−93.259750	1.0646	1.1670	3.3010	3467 (77.0)	2022 (0.2)	718 (72.2)
cc-pVQZ MP2	−93.282004	1.0642	1.1635	3.2851	3466 (77.0)	2037 (0.2)	722 (72.0)
aug-cc-pVQZ MP2	−93.284758	1.0645	1.1639	3.2976			
cc-pV5Z MP2	−93.292201	1.0640	1.1628	3.2953			
DZP CISD	−93.157909	1.0715	1.1636	3.0049	3528 (63.4)	2211 (1.9)	757 (82.8)
TZ2P CISD	−93.206779	1.0614	1.1443	3.0713	3501 (68.8)	2233 (1.5)	759 (73.6)
TZ3P CISD	−93.209281	1.0618	1.1465	3.0648	3504 (67.4)	2230 (1.4)	757 (70.1)
TZ2P(f,d) CISD	−93.232171	1.0603	1.1441	3.0814	3538 (70.9)	2250 (2.0)	797 (70.2)
TZ2P(f,d)+diff CISD	−93.232658	1.0606	1.1440	3.0912	3533 (70.5)	2249 (2.1)	797 (75.0)
TZ3P(2f,2d) CISD	−93.237827	1.0597	1.1428	3.0820	3518 (68.4)	2246 (2.1)	782 (68.1)
TZ3P(2f,2d)+2diff CISD	−93.238253	1.0599	1.1427	3.0959	3515 (69.4)	2246 (2.3)	784 (68.9)
6-311G(d,p) CISD	−93.183918	1.0648	1.1497	2.9814	3532 (66.5)	2233 (1.5)	801 (72.6)
6-311++G(d,p) CISD	−93.186309	1.0656	1.1501	3.0699	3524 (69.7)	2229 (2.1)	778 (81.2)
6-311G(3d,3p) CISD	−93.204330	1.0611	1.1452	2.9866	3509 (64.9)	2230 (1.4)	760 (63.4)
6-311++G(3d,3p) CISD	−93.206888	1.0616	1.1456	3.0851	3504 (68.2)	2226 (1.9)	764 (69.2)
cc-pVDZ CISD	−93.155536	1.0767	1.1606	2.8974	3526 (67.2)	2229 (1.9)	764 (70.1)
aug-cc-pVDZ CISD	−93.167895	1.0751	1.1603	3.0950	3500 (67.7)	2212 (1.7)	752 (72.8)
cc-pVTZ CISD	−93.231892	1.0609	1.1449	3.0448	3529 (66.3)	2245 (1.8)	777 (70.9)
aug-cc-pVTZ CISD	−93.236797	1.0610	1.1447	3.0995	3522 (70.6)	2243 (2.3)	780 (69.0)
cc-pVQZ CISD	−93.255459	1.0608	1.1413	3.0902	3522 (70.8)	2257 (2.2)	784 (69.2)
6-311G(d,p) CCD	−93.202271	1.0681	1.1552	2.9270	3492 (66.1)	2184 (0.3)	775 (72.1)
6-311++G(d,p) CCD	−93.204839	1.0687	1.1558	3.0221	3485 (69.5)	2179 (0.6)	749 (81.6)
6-311G(3d,3p) CCD	−93.224198	1.0645	1.1510	2.9380	3462 (64.1)	2178 (0.3)	730 (63.8)
6-311++G(3d,3p) CCD	−93.226891	1.0651	1.1514	3.0401	3458 (67.6)	2175 (0.5)	734 (69.6)
cc-pVTZ CCD	−93.253696	1.0644	1.1505	2.9979	3481 (65.5)	2195 (0.5)	748 (71.0)
aug-cc-pVTZ CCD	−93.259213	1.0646	1.1505	3.0585	3472 (69.9)	2192 (0.8)	750 (69.1)
cc-pVQZ CCD	−93.278430	1.0644	1.1469	3.0487	3473 (70.0)	2207 (0.8)	755 (69.3)
6-311G(d,p) QCISD	−93.207354	1.0689	1.1589	2.9246	3476 (59.7)	2149 (0.3)	767 (71.8)
6-311++G(d,p) QCISD	−93.210051	1.0696	1.1595	3.0265	3469 (62.2)	2144 (0.6)	738 (81.3)
6-311G(3d,3p) QCISD	−93.221665	1.0652	1.1543	2.9303	3448 (58.6)	2146 (0.2)	722 (63.4)
6-311++G(3d,3p) QCISD	−93.231944	1.0658	1.1548	3.0389	3444 (62.1)	2142 (0.5)	725 (69.6)
cc-pVTZ QCISD	−93.258461	1.0651	1.1540	2.9906	3468 (60.4)	2162 (0.5)	741 (71.1)
aug-cc-pVTZ QCISD	−93.268802	1.0652	1.1538	3.0525	3459 (64.7)	2160 (0.7)	742 (69.5)
cc-pVQZ QCISD	−93.283142	1.0650	1.1503	3.0405	3461 (65.1)	2175 (0.7)	747 (69.8)
DZP CCSD	−93.179628	1.0754	1.1723	2.9477	3475 (58.7)	2137 (0.3)	724 (82.2)
TZ2P CCSD	−93.230269	1.0653	1.1521	3.0200	3443 (64.4)	2162 (0.3)	724 (74.0)
TZ3P CCSD	−93.233000	1.0656	1.1544	3.0123	3448 (63.0)	2159 (0.2)	721 (70.8)
TZ2P(f,d) CCSD	−93.257429	1.0642	1.1519	3.0305	3482 (66.7)	2180 (0.5)	764 (70.8)
TZ2P(f,d)+diff CCSD	−93.257956	1.0644	1.1518	3.0425	3477 (66.5)	2180 (0.5)	763 (75.9)
TZ3P(2f,2d) CCSD	−93.263424	1.0637	1.1506	3.0318	3459 (64.5)	2176 (0.5)	746 (68.9)
TZ3P (2f,2d)+2diff CCSD	−93.263883	1.0639	1.1506	3.0475	3456 (65.5)	2176 (0.7)	748 (69.8)
cc-pVDZ CCSD	−93.177156	1.0809	1.1688	2.8317	3470 (61.4)	2157 (0.3)	732 (69.3)
aug-cc-pVDZ CCSD	−93.190783	1.0796	1.1688	3.0433	3442 (62.9)	2138 (0.3)	718 (73.3)
cc-pVTZ CCSD	−93.257250	1.0649	1.1528	2.9879	3472 (62.2)	2175 (0.4)	742 (71.4)
aug-cc-pVTZ CCSD	−93.262621	1.0650	1.1526	3.0493	3463 (66.7)	2173 (0.6)	744 (69.7)
DZP CCSD(T)	−93.191130	1.0769	1.1783	2.9097	3453 (56.5)	2084 (0.0)	701 (84.1)
TZ2P CCSD(T)	−93.246610	1.0673	1.1593	2.9793	3414 (61.7)	2098 (0.0)	697 (75.5)
TZ3P CCSD(T)	−93.249669	1.0676	1.1617	2.9714	3419 (60.3)	2095 (0.0)	692 (72.3)

TABLE 5: (Continued)

level of theory	energy	r_e(CH)	r_e(CN)	μ_e	$\omega_{1,\sigma^+}(I_1)$	$\omega_{2,\sigma^+}(I_2)$	$\omega_{3,\pi}(I_3)$
TZ2P(f,d) CCSD(T)	−93.275144	1.0660	1.1591	2.9872	3455 (64.3)	2116 (0.0)	738 (72.4)
TZ2P(f,d)+diff CCSD(T)	−93.275703	1.0663	1.1590	3.0006	3450 (64.4)	2116 (0.1)	737 (77.9)
TZ3P(2f,2d) CCSD(T)	−93.281760	1.0657	1.1579	2.9894	3429 (62.2)	2111 (0.1)	719 (70.4)
TZ3P (2f,2d)+2diff CCSD(T)	−93.282254	1.0659	1.1579	3.0061	3426 (63.4)	2111 (0.1)	721 (71.4)
cc-pVDZ CCSD (T)	−93.189560	1.0826	1.1753	2.7855	3447 (58.0)	2098 (0.0)	708 (70.7)
aug-cc-pVDZ CCSD (T)	−93.204711	1.0816	1.1758	3.0050	3415 (60.0)	2077 (0.0)	693 (75.3)
cc-pVTZ CCSD (T)	−93.275219	1.0668	1.1601	2.9401	3443 (59.9)	2111 (0.0)	716 (72.9)
aug-cc-pVTZ CCSD (T)	−93.281168	1.0671	1.1601	3.0076	3433 (64.4)	2108 (0.1)	717 (71.3)
expt.[a]		1.06549	1.15321				
expt.[b]		1.06501	1.15324				
expt.[c]				2.985			
expt.[d]					3442	2129	727
expt.[e]					3440	2128	727
expt.[f]					3442	2127	727
expt.[g]					3444	2130	725
expt.[h]					(53.3)	−	(57.7)
expt.[i]					(54)	(0.1)	(46)

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A. Equilibrium Geometries. The influence of basis sets and theoretical method employed on the quality of geometry predictions may be followed by surveying Tables 1−6. In Table 7, the percentage deviations between observed and theoretically estimated bond lengths at the different levels of theory and selected basis sets are given. The data illustrate quite clearly the improvements in consistency between the theory and experiment with more complete descriptions of electron correlation. The inclusion of diffuse functions in the basis sets does not appear to affect in any significant way the theoretically estimated bond lengths of these neutral molecules. Due to fortuitous cancellation of errors, the best overall agreement for the bond lengths among the molecules studied is achieved using the QCISD method. The average error over all molecules studied for 6-311++G(3d,3p) QCISD computations is 0.18%. For the aug-cc-pVTZ QCISD results the average percentage error is 0.16%. At the aug-cc-pVTZ QCISD level of theory the OH bond length in H_2O is predicted to be 0.9591 Å. At the cc-pVQZ QCISD level the theoretical value is 0.9556 Å. Notably, cc-pVQZ CCSD(T) computations for H_2O produce a OH bond length of 0.9578 Å (Table 1), in perfect accord with experiment. At the MP2 level, computations employing the Dunning's cc-pVQZ and aug-cc-pVQZ basis sets were performed. The overall agreement between theory and experiment is improved compared to the respective triple-ζ type basis set results. The cost of such computations at the higher correlated levels of theory is quite considerable. Table 8 shows the percentage errors for the theoretical equilibrium bond angles. Excellent agreement between theory and experiment is obtained for several basis sets at the QCISD and CCSD(T) levels. At these levels of theory, the inclusion of diffuse functions in the basis set clearly improves the accord between theory and experiment. Both aug-cc-pVTZ and cc-pVQZ QCISD computations lead to a predicted bond angle for water of 104.35 degrees, in very good accord with the experimental value of 104.5 degrees. The respective results for aug-cc-pVTZ and cc-pVQZ CCSD(T) computations are, 104.18 and 104.12 degrees, respectively.

It should be emphasized that the experimental data depend on the accuracy of the spectroscopic measurements as well as on the approximations inherent in the model potential employed in fitting the experimental data.

B. Dipole Moments. The percentage deviations of the theoretically estimated dipole moments from the experimentally determined values are illustrated in Table 9. It should be underlined that the experimental dipole moments represent in fact μ_o values that do not coincide with the theoretical μ_e values. The μ_o dipole moments are measured from Stark shifts and require a transition from one rotational state to another. Therefore, μ_o does not usually refer to the rotational ground state. Thus, the direct comparison between theory and experiment is necessarily approximate. Nevertheless, two definite conclusions can be made from the data presented (Table 9): (a) Good overall agreement between theory and experiment is obtained from computations at the correlated levels of theory QCISD, CCSD, and CCSD(T); (b) The best accord between theory and experiment is obtained at the CCSD(T) level with triple-ζ type basis sets that include diffuse functions [TZ3P-(2f,2d)+2diff] and aug-cc-pVTZ. For CCSD(T) computations employing the latter basis sets the estimated dipole moments compare quite favorably with the experimental values. In the case of H_2O the theoretical dipole moments are: 1.8475 D for TZ3P(2f,2d)+diff and 1.8453 D for aug-cc-VTZ basis sets. The experimental μ_e value is 1.8473 D (Table 1). For H_2CO, the estimated dipole moment values for the same levels of theory are 2.3886 and 2.3935 D, respectively. The experimental value is 2.331 D (Table 3). For HCN the respective predicted values are 3.0061 and 3.0076 D, whereas the experimental dipole moment is 2.985 D (Table 5).

C. Harmonic Vibrational Frequencies. In Tables 1−6, the theoretically predicted harmonic vibrational frequencies for the six studied molecules are compared with the respective experimental values. At the SCF level, the effects of basis set quality may best be followed in the case of the water molecule (Table 1). The results include data for computations employing very large basis sets of the Dunning's correlation consistent type. The Hartree−Fock limit is reached at the cc-pVQZ SCF level. Further increases in the size of basis set do not lead to any significant improvement of the theoretical results. At the Hartree−Fock level of theory the predicted harmonic frequencies for the fundamental vibrational modes are estimated at above the experimental values. Interestingly, the percentage deviations above the experimental values vary quite considerably between different modes in a molecule and between the different

TABLE 6: Theoretical Predictions of the Total Energy (in hartree), Geometrical Parameter (bond length in Å), Harmonic Vibrational Frequencies (in Cm^{-1}), and Infrared Intensities (in parentheses in Km mol^{-1}) for the SiH_4 Molecule

level of theory	energy	r_e	$\omega_{1,a_1}(I_1)$	$\omega_{2,e}(I_2)$	$\omega_{3,t_2}(I_3)$	$\omega_{4,t_2}(I_4)$
DZ SCF	−291.180715	1.4830	2305 (0)	1055 (0)	2293 (475.4)	983 (669.1)
TZ SCF	−291.200346	1.4847	2273 (0)	1044 (0)	2261 (402.2)	978 (668.3)
DZP SCF	−291.234602	1.4743	2361 (0)	1060 (0)	2346 (451.4)	1028 (687.1)
TZ2P SCF	−291.256843	1.4744	2329 (0)	1046 (0)	2316 (477.8)	1011 (588.3)
TZ3P SCF	−291.258698	1.4742	2343 (0)	1046 (0)	2329 (472.8)	1011 (539.1)
TZ2P(f,d) SCF	−291.258881	1.4752	2335 (0)	1043 (0)	2321 (493.9)	1011 (597.8)
TZ2P(f,d)+diff SCF	−291.258910	1.4752	2335 (0)	1043 (0)	2321 (499.1)	1011 (599.1)
TZ3P(2f,2d) SCF	−291.260184	1.4743	2337 (0)	1043 (0)	2322 (479.7)	1010 (539.6)
TZ3P(2f,2d)+2diff SCF	−291.260221	1.4743	2336 (0)	1044 (0)	2322 (485.9)	1010 (541.0)
6-311G(d,p) SCF	−291.253175	1.4773	2351 (0)	1051 (0)	2338 (516.3)	1019 (704.3)
6-311++G(d,p) SCF	−291.253312	1.4773	2351 (0)	1051 (0)	2337 (522.2)	1019 (705.4)
6-311G(3d,3p) SCF	−291.258524	1.4745	2341 (0)	1046 (0)	2326 (472.9)	1010 (539.1)
6-311++G(3d,3p) SCF	−291.258563	1.4745	2341 (0)	1046 (0)	2326 (478.9)	1010 (541.9)
cc-pVDZ SCF	−291.242909	1.4862	2320 (0)	1039 (0)	2311 (478.6)	999 (587.5)
aug-cc-pVDZ SCF	−291.243246	1.4865	2310 (0)	1035 (0)	2301 (466.3)	991 (527.0)
cc-pVTZ SCF	−291.260573	1.4782	2329 (0)	1042 (0)	2318 (493.6)	1007 (554.6)
aug-cc-pVTZ SCF	−291.260860	1.4781	2329 (0)	1042 (0)	2319 (486.8)	1006 (540.1)
cc-pVQZ SCF	−291.266070	1.4755	2335 (0)	1044 (0)	2321 (484.0)	1010 (551.7)
6-311G(d,p) MP2	−291.371926	1.4745	2330 (0)	1017 (0)	2335 (405.3)	973 (595.3)
6-311++G(d,p) MP2	−291.372336	1.4745	2330 (0)	1007 (0)	2334 (413.1)	973 (597.2)
6-311G(3d,3p) MP2	−291.387139	1.4734	2304 (0)	1007 (0)	2307 (370.3)	956 (472.8)
6-311++G(3d,3p) MP2	−291.387398	1.4733	2303 (0)	1008 (0)	2307 (376.7)	956 (475.4)
cc-pVDZ MP2	−291.335931	1.4869	2283 (0)	1001 (0)	2294 (349.2)	946 (475.8)
cc-pVTZ MP2	−291.403771	1.4774	2296 (0)	1004 (0)	2303 (363.7)	951 (461.6)
aug-cc-pVTZ MP2	−291.406632	1.4779	2293 (0)	1002 (0)	2299 (366.0)	947 (451.5)
DZP CISD	−291.373107	1.4717	2335 (0)	1022 (0)	2337 (353.9)	987 (582.0)
TZ2P CISD	−291.407313	1.4749	2281 (0)	1012 (0)	2279 (364.6)	963 (503.7)
TZ3P CISD	−291.409453	1.4742	2293 (0)	1004 (0)	2293 (376.7)	957 (467.4)
TZ2P(f,d) CISD	−291.422234	1.4760	2290 (0)	1002 (0)	2291 (369.7)	953 (487.7)
TZ2P(f,d)+diff CISD	−291.422299	1.4761	2290 (0)	1000 (0)	2290 (373.9)	952 (488.7)
TZ3P(2f,2d) CISD	−291.426119	1.4751	2291 (0)	1001 (0)	2292 (367.1)	953 (446.9)
TZ3P(2f,2d)+2diff CISD	−291.426260	1.4751	2291 (0)	1000 (0)	2292 (372.0)	954 (447.7)
6-311G(d,p) CISD	−291.394131	1.4749	2317 (0)	1010 (0)	2320 (405.2)	971 (592.1)
6-311++G(d,p) CISD	−291.394591	1.4751	2316 (0)	1002 (0)	2318 (412.4)	971 (593.5)
6-311G(3d,3p) CISD	−291.409322	1.4746	2289 (0)	1001 (0)	2290 (377.3)	955 (468.1)
6-311++G(3d,3p) CISD	−291.409598	1.4745	2289 (0)	1003 (0)	2290 (382.9)	955 (470.1)
cc-pVDZ CISD	−291.383261	1.4878	2269 (0)	993 (0)	2277 (350.5)	943 (473.4)
aug-cc-pVDZ CISD	−291.389102	1.4895	2252 (0)	983 (0)	2259 (367.5)	930 (446.3)
cc-pVTZ CISD	−291.424598	1.4790	2282 (0)	1000 (0)	2286 (370.9)	951 (455.3)
aug-cc-pVTZ CISD	−291.426940	1.4793	2281 (0)	998 (0)	2283 (369.8)	947 (442.1)
6-311G(d,p) CCD	−291.399874	1.4759	2305 (0)	1005 (0)	2311 (393.4)	964 (581.3)
6-311++G(d,p) CCD	−291.400360	1.4759	2306 (0)	995 (0)	2311 (401.0)	964 (582.8)
6-311G(3d,3p) CCD	−291.416297	1.4763	2273 (0)	994 (0)	2276 (370.7)	947 (460.6)
6-311++G(3d,3p) CCD	−291.387398	1.4733	2303 (0)	1008 (0)	2307 (376.7)	956 (475.4)
cc-pVDZ CCD	−291.389418	1.4892	2256 (0)	986 (0)	2267 (336.4)	936 (463.4)
aug-cc-pVDZ CCD	−291.395919	1.4914	2236 (0)	974 (0)	2245 (359.7)	921 (438.6)
cc-pVTZ CCD	−291.403771	1.4774	2296 (0)	1004 (0)	2303 (363.7)	951 (461.6)
aug-cc-pVTZ CCD	−291.406632	1.4779	2293 (0)	1002 (0)	2299 (366.0)	947 (451.5)
6-311G(d,p) QCISD	−291.400861	1.4766	2299 (0)	1001 (0)	2304 (388.6)	961 (571.6)
6-311G(3d,3p) QCISD	−291.411479	1.4768	2268 (0)	990 (0)	2270 (362.2)	943 (450.9)
6-311++G(3d,3p) QCISD	−291.417626	1.4770	2267 (0)	992 (0)	2269 (368.0)	943 (452.7)
cc-pVDZ QCISD	−291.390419	1.4899	2250 (0)	982 (0)	2260 (331.9)	931 (452.6)
aug-cc-pVDZ QCISD	−291.396933	1.4920	2331 (0)	971 (0)	2239 (352.0)	917 (428.8)
cc-pVTZ QCISD	−291.433648	1.4816	2259 (0)	989 (0)	2265 (352.6)	938 (434.6)
DZP CCSD	−291.379455	1.4730	2321 (0)	1014 (0)	2324 (337.0)	979 (563.8)
TZ2P CCSD	−291.415293	1.4771	2260 (0)	1003 (0)	2260 (348.5)	953 (487.0)
TZ3P CCSD	−291.417357	1.4764	2272 (0)	994 (0)	2273 (362.3)	946 (451.5)
TZ2P(f,d) CCSD	−291.431079	1.4785	2269 (0)	992 (0)	2271 (352.6)	941 (467.9)
TZ2P(f,d)+diff CCSD	−291.431146	1.4786	2269 (0)	990 (0)	2270 (357.1)	941 (469.0)
TZ3P(2f,2d) CCSD	−291.435077	1.4777	2269 (0)	990 (0)	2272 (350.9)	942 (428.1)
TZ3P(2f,2d)+2diff CCSD	−291.435226	1.4777	2269 (0)	990 (0)	2272 (356.0)	942 (429.0)
cc-pVDZ CCSD	−291.390342	1.4898	2251 (0)	983 (0)	2260 (332.0)	932 (454.2)
aug-cc-pVDZ CCSD	−291.396849	1.4919	2231 (0)	971 (0)	2240 (352.6)	918 (430.3)
cc-pVTZ CCSD	−291.433525	1.4815	2260 (0)	989 (0)	2266 (353.1)	939 (436.2)
aug-cc-pVTZ CCSD	−291.436025	1.4819	2258 (0)	987 (0)	2262 (353.2)	935 (423.0)
DZP CCSD(T)	−291.381685	1.4738	2313 (0)	1009 (0)	2317 (329.2)	973 (550.2)
TZ2P CCSD(T)	−291.418424	1.4781	2252 (0)	999 (0)	2253 (336.7)	947 (472.1)
TZ3P CCSD(T)	−291.420564	1.4775	2262 (0)	989 (0)	2265 (350.2)	939 (438.9)
TZ2P(f,d) CCSD(T)	−291.434774	1.4795	2260 (0)	986 (0)	2264 (338.1)	932 (451.6)
TZ2P(f,d)+diff CCSD(T)	−291.434843	1.4795	2259 (0)	983 (0)	2263 (342.9)	932 (452.8)
TZ3P(2f,2d) CCSD(T)	−291.439041	1.4787	2260 (0)	984 (0)	2264 (336.3)	933 (414.3)
TZ3P(2f,2d)+2diff CCSD(T)	−291.439196	1.4787	2260 (0)	984 (0)	2264 (341.5)	933 (415.2)
cc-pVDZ CCSD(T)	−291.392803	1.4908	2242 (0)	978 (0)	2254 (323.8)	926 (440.6)
aug-cc-pVDZ CCSD(T)	−291.399764	1.4930	2221 (0)	966 (0)	2232 (343.6)	910 (418.9)
cc-pVTZ CCSD(T)	−291.437350	1.4825	2251 (0)	984 (0)	2258 (338.0)	931 (420.3)
aug-cc-pVTZ CCSD(T)	−291.440069	1.4830	2248 (0)	981 (0)	2255 (338.7)	925 (408.7)
Expt.[a]		1.47313				
Expt.[b,c]			2268	960	2273	929
Expt.[d]					(281.6)	(381.3)

[a] Ohno, K.; Matsuura, H.; Endo, Y.; Hirota, E. *J. Mol. Spectrosc*. **1986**, *118*, 1. [b] Kattenberg, H. W.; Oskam, A. *J. Mol. Spectrosc*. **1974**, *49*, 52. [c] Allen, W. D.; Schaefer, H. F. *Chem. Phys*. **1986**, *108*, 243. [d] Coats, A. M.; McKean, D. C.; Steele, D. *J. Mol. Struct*. **1994**, *320*, 269.

TABLE 7: Percentage Errors for Theoretical Equilibrium Bond Lengths (R_e)[a]

			H_2CO		C_2H_2		HCN		
level of theory	H_2O r_e(OH)	CH_4 r_e(CH)	r_e(CH)	r_e(CO)	r_e(CH)	r_e(CC)	r_e(CH)	r_e(CN)	SiH_4 r_e (SiH)
TZ3P(2f,2d) SCF	−1.80	−0.37	−0.59	1.78	−0.77	−1.90	−1.06	−2.55	0.08
TZ3P(2f,2d)+2diff SCF	−1.79	−0.37	−0.59	−2.13	−0.81	−1.90	−0.84	−2.54	0.08
6-311G(3d,3p) SCF	−1.81	−0.37	−0.57	−2.19	−0.76	−1.90	−0.86	−2.54	0.09
6-311++G(3d,3p) SCF	−1.78	−0.37	−0.61	−2.08	−0.76	−1.78	−0.83	−2.48	0.09
cc-pVTZ SCF	−1.59	−0.34	−0.55	−1.94	−0.76	−1.82	−0.84	−2.47	0.35
aug-cc-pVTZ SCF	−1.69	−0.34	−0.57	−2.04	−0.76	−1.81	−0.82	−2.50	0.34
6-311G(3d,3p) MP2	0.08	−0.01	0.13	0.57	0.27	1.18	−0.13	1.16	0.02
6-311++G(3d,3p) MP2	0.20	0.0	0.07	0.76	−0.12	0.94	−0.07	1.21	0.01
cc-pVTZ MP2	0.20	−0.05	0.14	0.62	−0.06	0.76	−0.11	1.18	0.29
aug-cc-pVTZ MP2	0.44	0.03	0.11	0.82	0.03	0.85	−0.08	1.20	0.33
cc-pVQZ MP2	0.05	−0.17	0.02	0.43	−0.08	0.55	−0.12	0.89	−
aug-cc-pVQZ MP2	0.17	−	0.03	0.53	−	−	−0.09	0.93	−
TZ3P(2f,2d) CISD	−0.56	−0.17	−0.39	−0.70	−0.40	−0.66	−0.54	−0.90	0.14
TZ3P(2f,2d)+2diff CISD	−0.54	−0.17	0.71	0.47	−0.41	−0.71	−0.53	−0.91	0.14
6-311G(3d,3p) CISD	−0.43	0.04	−0.17	−0.66	−0.32	−0.47	−0.41	−0.69	0.10
6-311++G(3d,3p) CISD	−0.38	0.04	−0.22	−0.53	−0.30	1.08	−0.37	−0.66	0.10
cc-pVTZ CISD	−0.37	−0.06	−0.23	−0.64	−0.34	−0.50	−0.43	−0.72	0.40
aug-cc-pVTZ CISD	−0.25	0.01	−0.25	−0.55	−0.33	−0.47	−0.56	−0.74	0.42
6-311G(3d,3p) CCD	−0.17	0.22	0.20	−0.27	−0.02	0	−0.09	0.10	0.22
6-311++G(3d,3p) CCD	−0.11	0.23	0.15	−0.12	0.02	0.02	0.03	0.14	0.01
cc-pVTZ CCD	−0.09	0.14	0.15	−0.24	−0.12	−0.03	−0.10	−0.23	0.29
aug-cc-pVTZ CCD	0.07	0.21	0.15	−0.12	−0.08	−0.02	−0.08	−0.23	0.33
6-311G(3d,3p) QCISD	−0.04	0.28	0.30	0.11	0.05	0.22	−0.03	0.10	0.25
6-311++G(3d,3p) QCISD	0.04	0.29	0.25	0.27	0.06	0.32	0.03	0.14	0.26
cc-pVTZ QCISD	0.02	0.19	0.25	0.13	0.0	0.18	−0.04	0.07	0.57
aug-cc-pVTZ QCISD	0.20	0.27	0.22	0.26	0.01	0.21	−0.03	0.05	−
TZ3P(2f,2d) CCSD	−0.18	0.05	0.03	−0.02	−0.07	−0.07	−0.17	−0.22	0.31
TZ3P(2f,2d)+2diff CCSD	−0.16	0.06	0.02	0.0	−0.12	−0.07	−0.15	−0.22	0.31
cc-pVTZ CCSD	−0.01	0.17	0.19	0.0	0.0	−0.07	−0.06	−0.03	0.57
aug-cc-pVTZ CCSD	0.16	0.25	0.17	0.12	−0.05	0.13	−0.05	−0.05	0.60
TZ3P(2f,2d) CCSD(T)	0.08	0.17	0.21	0.56	0.05	0.47	0.02	0.41	0.38
TZ3P(2f,2d)+2diff CCSD(T)	0.13	0.17	0.21	0.58	0.05	0.47	0.04	0.41	0.38
cc-pVTZ CCSD(T)	−0.25	0.29	0.39	0.66	0.10	0.64	0.12	0.60	0.64
aug-cc-pVTZ CCSD(T)	0.46	0.38	0.37	0.71	0.13	0.67	0.15	0.60	0.67

[a] A negative sign means that the theoretical value is less than the experimental distance.

molecules studied. The variations are from 2.5% to 30% in particular modes in some molecules (Tables 10 and 11).

Quite realistic frequency values for some molecules are predicted by the MP2 theory employing basis sets of the type 6-311G(3d,3p), 6-311++G(3d,3p), cc-pVTZ, and aug-cc-pVTZ. The maximum deviations from the experimental values for H_2O, CH_4, H_2CO, and SiH_4 are less than 2% (Tables 10 and 11). For acetylene and hydrogen cyanide, however, the errors in the theoretical frequencies for one particular vibrational mode are quite sizable. This is the case with ω_4 bending mode for HCCH and the C≡N stretching mode (ω_2) of HCN. The frequencies of all other modes in these molecules are evaluated within the 3% range. Notably, computations employing the Dunning's cc-pVTZ and aug-cc-pVTZ basis sets produce better results for the frequencies of the latter two modes (Table 11). Quite good accord between theoretical and experimental vibrational frequencies is obtained by CCD/extended basis set computations.

At the higher correlated QCISD, CCSD and CCSD(T) levels the consistency between experiment and theory is further improved. For these methods, the largest basis sets used consistently for all molecules were of triple-ζ type. Again, computations involving the cc-pVTZ and aug-cc-pVTZ basis sets produced best overall accord between theoretical and experimental frequencies. The average error for the theoretical frequencies at the QCISD/cc-pVTZ level for all modes of the six molecules studied is 1.0%. Inclusion of diffuse functions slightly improves the results. The average error for QCISD/aug-cc-pVTZ computations is 0.9%. At the cc-pVTZ CCSD level, the average error is 1.1% while for aug-cc-pVTZ CCSD computations it is 1.0%. At the CCSD(T) level the overall accuracy of predicting is affected by the underestimated harmonic frequency for the ω_4 bending mode of acetylene. The percentage errors for this particular vibration are −11.2% for the TZ3P(2f,2d) basis set, −7.4% for the cc-pVTZ and −5.0% for the aug-cc-pVTZ computations. The application of the Dunning's correlation consistent basis sets of triple-ζ type and the inclusion of diffuse functions improves in all cases the consistency between theoretically estimated and experimental frequencies. It is indeed quite significant that for the QCISD, CCSD, and CCSD(T) methods combined with triple-ζ type of basis sets that includes diffuse functions, the agreement between theoretical and experimental harmonic vibrational frequencies is estimated with an average error per molecule of maximum 1.5%. The best accord is obtained from Dunning's correlation consistent basis sets. Comparisons between the above three methods employing larger basis sets were obtained for the H_2O molecule. For the cc-pVQZ QCISD computations, the deviations for the theoretical ω_1, ω_2, and ω_3 fundamental harmonic frequencies are 1.2% (47 cm^{-1}), 1.3% (22 cm^{-1}) and 1.1% (41 cm^{-1}), respectively. For the cc-pVQZ CCSD computations the percentage errors for the ω_1, ω_2, and ω_3 fundamental modes are 1.4% (63 cm^{-1}), 1.3% (22 cm^{-1}) and 1.1% (56 cm^{-1}). Far superior predictions are achieved by the cc-pVQZ CCSD(T) computations with errors equal to 0.3% (12 cm^{-1}), 0.6% (10 cm^{-1}) and 0.2% (8 cm^{-1}), for the three modes, respectively.

D. Infrared Intensities. It has been recognized that quantitative predictions by ab initio methods of the intensities associated with the infrared spectra of molecules are particularly difficult to achieve.[1,3,7] As a property, the infrared band intensities are determined by two principle factors: (a) the fluctuations of the intramolecular electric charges accompanying particular vibrational modes; (b) the forms of the vibrations as represented by the vibrational eigenvectors. Therefore, reliable theoretical estimates of IR intensities can be expected from computations

TABLE 8: Percentage Errors for Theoretical Equilibrium Bond Angles (θ_e)[a]

level of theory	H_2O θ_e(HOH)	H_2CO θ_e(HCH)
TZ3P(2f,2d) SCF	1.71	−0.37
TZ3P(2f,2d)+2diff SCF	1.77	−0.33
6-311G(3d,3p) SCF	1.22	−0.39
6-311++G(3d,3p) SCF	1.64	−0.25
cc-pVTZ SCF	1.44	−0.48
aug-cc-pVTZ SCF	1.73	−0.33
6-311G(3d,3p) MP2	−0.56	−0.23
6-311++G(3d,3p) MP2	−0.02	0.01
cc-pVTZ MP2	−0.96	−0.28
aug-cc-pVTZ MP2	−0.37	0.08
cc-pVQZ MP2	−0.47	−0.05
aug-cc-pvQZ MP2	−0.23	0.11
TZ3P(2f,2d) CISD	0.29	−0.12
TZ3P(2f,2d)+2diff CISD	0.36	−0.25
6-311G(3d,3p) CISD	−0.02	−0.33
6-311++G(3d,3p) CISD	−0.56	−0.15
cc-pVTZ CISD	−0.32	−0.33
aug-cc-pVTZ CISD	0.26	−0.09
6-311G(3d,3p) CCD	−0.18	−0.22
6-311++G(3d,3p) CCD	0.36	−0.03
cc-pVTZ CCD	−0.49	−0.24
aug-cc-pVTZ CCD	−0.01	0.02
6-311G(3d,3p) QCISD	−0.41	−0.32
6-311++G(3d,3p) QCISD	0.20	−0.11
cc-pVTZ QCISD	−0.62	−0.33
aug-cc-pVTZ QCISD	−0.14	−0.05
TZ3P(2f,2d) CCSD	0.01	−0.03
TZ3P(2f,2d)+2diff CCSD	0.10	0.05
cc-pVTZ CCSD	−0.58	−0.28
aug-cc-pVTZ CCSD	−0.07	0.0
TZ3P(2f,2d) CCSD(T)	−0.22	0.03
TZ3P(2f,2d)+2diff CCSD(T)	−0.14	0.11
cc-pVTZ CCSD(T)	−0.88	−0.27
aug-cc-pVTZ CCSD(T)	−0.31	0.06

[a] A negative sign means that the theoretical value is less than the experimental angle.

TABLE 9: Percentage Errors for Theoretical Equilibrium Dipole Moment (μ_e) from Experimental Dipole Moment (μ_o)[a]

level of theory	H_2O μ_e	H_2CO μ_e	HCN μ_e
TZ3P(2f,2d) SCF	4.46	15.36	8.89
TZ3P(2f,2d)+2diff SCF	4.96	16.64	9.34
6-311G(3d,3p) SCF	1.40	−10.90	6.84
6-311++G(3d,3p) SCF	6.88	17.50	9.56
cc-pVTZ SCF	7.61	14.24	8.10
aug-cc-pVTZ SCF	4.99	16.93	9.31
6-311G(3d,3p) MP2	3.74	18.29	7.96
6-311++G(3d,3p) MP2	9.24	25.17	10.84
cc-pVTZ MP2	10.57	21.30	9.26
aug-cc-pVTZ MP2	7.87	24.60	10.59
cc-pVQZ MP2	9.11	22.47	10.05
aug-cc-pvQZ MP2	7.50	23.66	10.47
TZ3P(2f,2d) CISD	0.92	6.01	3.25
TZ3P(2f,2d)+2diff CISD	1.52	7.50	3.72
6-311G(3d,3p) CISD	−3.36	−0.08	0.05
6-311++G(3d,3p) CISD	3.48	7.10	3.35
cc-pVTZ CISD	4.88	3.52	2.00
aug-cc-pVTZ CISD	1.53	7.76	3.84
6-311G(3d,3p) CCD	−3.62	−3.30	−1.57
6-311++G(3d,3p) CCD	3.35	4.19	−
cc-pVTZ CCD	4.66	0.26	0.43
aug-cc-pVTZ CCD	1.48	4.90	2.46
6-311G(3d,3p) QCISD	−4.43	−3.29	−1.83
6-311++G(3d,3p) QCISD	2.74	4.51	1.81
cc-pVTZ QCISD	4.25	0.31	0.19
aug-cc-pVTZ QCISD	0.66	5.12	2.26
TZ3P(2f,2d) CCSD	0.26	2.78	1.57
TZ3P(2f,2d)+2diff CCSD	0.89	4.77	2.09
cc-pVTZ CCSD	4.31	0.29	0.10
aug-cc-pVTZ CCSD	1.51	4.99	2.15
TZ3P(2f,2d) CCSD(T)	−0.64	1.06	0.15
TZ3P(2f,2d)+2diff CCSD(T)	0.01	2.82	0.71
cc-pVTZ CCSD(T)	3.66	−2.17	−1.50
aug-cc-pVTZ CCSD(T)	−0.11	3.03	0.76

[a] A negative sign means that the theoretical value is less than the experimental dipole moment.

that provide an accurate description of the electronic charge density and its dynamics with vibrational distortions. An accurate theoretical force field is also needed in order to obtain reliable vibrational eigenvectors. It should be underlined that the simultaneous theoretical prediction of vibrational frequencies and infrared intensities may be considered as an important all-round criterion for the accuracy of the molecular wave functions.

On the experimental side, there are a number of problems hampering the accurate determination of absolute infrared intensities in the gas-phase: (a) difficulties in separating overlapped bands; (b) possible influences of the rotational fine structure on the measured band intensities; (c) effects of the instrument function over the intensity values determined. It has been estimated that an overall error of about 10−15% is usually present in the experimentally determined gas-phase infrared band intensities.[1,7] To the above, we should add that the experimental IR intensities usually include anharmonic effects that are not present in the theoretically predicted quantities. The reported differences in intensity values in the literature suggest even higher possible errors for some molecules. The accuracy of experimental measurements is improving in recent years with advances in spectroscopic technology as well as the development of sophisticated software for band deconvolution, separation, and spectral curve fitting.

The comparisons between infrared intensities predicted at different levels of theory and the respective experimental quantities for the six molecules studied may be followed in Tables 1−6. The survey shows that satisfactory accord between experiment and theory can be achieved by methods that account most fully for the effects of electron correlation. At the SCF level, using even quite large basis sets, the discrepancy between theory and experiment is drastic. This is clearly seen in the case of the H_2O molecule (Table 1). Aug-cc-pV5Z SCF computations lead to intensity values that differ by several hundred percent for the ω_1 mode, 51% for ω_2 mode and 122% for the ω_3 mode as compared to the most recent experimental data of Rothman et al. (ref. g, footnotes of Table 1). At the MP2, CISD, and CCD levels, the theoretical results become closer to the experimental values for all molecules. At the CCSD level of theory employing triple-ζ types of basis sets the agreement between theoretical and experimental IR intensities can be considered quite satisfactory. The effect of size of basis set on the quality of intensity prediction does not appear strictly systematic. In the case of water, the best accord between theory and experiment is fortuitously obtained from aug-cc-pVDZ CCSD computations (Table 1). The average error in the predicted intensities is just 8.4% with maximum deviation of 16.4% for the ω_3 mode. Applying the larger basis sets cc-pVTZ, aug-cc-pVTZ, and cc-pVQZ appears to reduce the quality of intensity predictions at this level of theory. For most other molecules, however, such a tendency is not confirmed (Tables 2−6).

The comparisons of accuracies of theoretical predictions for the SCF, MP2, CISD, CCD, QCISD, CCSD, and CCSD(T) levels of theory employing cc-pVTZ and aug-cc-pVTZ basis sets is illustrated in Table 12. The best overall accord between theoretical and experimental data for all molecules studied is achieved at the CCSD(T) level of theory. Satisfactory results are also obtained from CCSD and QCISD computations. These methods also produced the best theoretical estimates for molecular geometries, dipole moment and harmonic vibrational frequencies. The effects of basis set size and type are not always well expressed. Studying the results for the six molecules reveals

TABLE 10: Percentage Errors for Theoretical Harmonic Vibrational Frequencies for H_2O, CH_4, and H_2CO[a]

	H_2O			CH_4				H_2CO					
level of theory	ω_1	ω_2	ω_3	ω_1	ω_2	ω_3	ω_4	ω_1	ω_2	ω_3	ω_4	ω_5	ω_6
SCF													
TZ3P(2f,2d)	7.59	9.61	7.13	4.06	5.24	2.88	6.29	4.82	12.98	5.57	12.34	4.89	6.44
TZ3P(2f,2d)+2diff	7.57	5.88	7.13	4.06	5.24	2.88	6.29	4.82	12.87	5.50	12.26	4.89	6.29
cc-pVTZ	7.70	6.31	7.20	4.03	5.24	2.82	6.36	4.75	13.32	5.69	12.26	4.78	6.37
aug-cc-pVTZ	7.54	5.82	7.10	4.03	5.24	2.82	6.29	4.86	12.92	5.44	12.09	4.85	6.13
MP2													
6-311G(3d,3p)	0.31	−1.21	1.52	1.12	0.88	1.11	−0.07	0.34	−0.28	−0.90	1.18	0.47	−1.24
6-311++G(3d,3p)	−0.02	−1.39	0.35	1.06	0.88	1.08	−0.15	0.61	−0.91	−1.15	0.59	0.90	−1.09
cc-pVTZ	0.60	0.18	0.81	1.68	0.19	1.77	−1.24	0.88	0.45	−0.64	1.51	1.13	−0.62
aug-cc-pVTZ	−0.26	−1.27	0.13	1.42	0.13	1.87	−1.17	0.99	−0.62	−1.47	0.59	1.30	−1.63
CISD													
TZ3P(2f,2d)	2.30	2.12	2.03	1.88	1.07	1.46	0.88	2.62	6.18	1.41	4.62	2.82	2.02
TZ3P(2f,2d)+2diff	2.17	2.00	2.03	1.85	1.07	1.33	0.88	2.62	6.06	1.28	4.37	2.79	1.79
cc-pVTZ	2.61	2.49	2.23	1.82	0.82	1.30	0.22	2.51	6.86	1.73	5.12	2.59	2.02
aug-cc-pVTZ	2.19	1.39	1.90	1.65	1.01	1.14	0.73	2.61	6.29	1.09	4.53	2.69	1.32
CCD													
6-311G(3d,3p)	1.15	1.82	0.86	0.36	0.69	−0.06	0.51	0.06	4.20	−0.06	1.93	0.17	−0.07
6-311++G(3d,3p)	1.07	0.55	0.94	0.36	0.69	−0.10	0.44	0.27	3.80	−0.32	1.43	0.50	0.07
cc-pVTZ	1.57	1.94	1.32	0.99	1.01	0.63	−0.73	0.71	5.05	0.19	2.52	0.96	0.62
aug-cc-pVTZ	0.97	0.79	0.84	0.79	0.19	0.44	0.52	0.78	4.31	−0.58	1.76	1.03	−0.31
QCISD													
6-311G(3d,3p)	0.57	1.64	0.26	0.10	0.50	−0.44	0.29	−0.44	2.10	−0.77	1.26	−0.56	−0.85
6-311++G(3d,3p)	0.39	0.30	0.30	0.07	0.51	−0.48	0.22	−0.20	1.59	−1.02	0.67	−0.17	−0.70
cc-pVTZ	1.04	1.76	0.81	0.73	−0.13	0.25	−0.80	0.27	3.00	−0.38	1.85	0.27	0.08
aug-cc-pVTZ	0.39	0.55	0.25	0.53	0.06	0.06	−0.29	0.37	2.21	−1.15	1.09	0.40	−1.01
CCSD													
TZ3P(2f,2d)	0.73	1.39	0.58	0.89	0.19	0.41	−0.15	0.61	2.89	−0.51	1.43	0.80	0.08
TZ3P(2f,2d)+2diff	0.55	1.21	0.46	0.86	0.13	0.38	−0.15	0.61	2.72	−0.70	1.18	0.80	−0.16
cc-pVTZ	1.15	1.76	0.91	0.83	−0.13	0.35	−0.80	0.48	3.74	−0.13	2.02	0.56	0.16
aug-cc-pVTZ	0.55	0.61	0.41	0.62	0.06	0.16	−0.29	0.58	3.00	−0.90	1.26	0.70	−0.70
CCSD(T)													
TZ3P(2f,2d)	−0.39	0.61	−0.41	0.33	−0.51	−0.06	−1.10	−0.37	0.0	−1.73	−0.59	−0.17	−1.24
TZ3P(2f,2d)+2diff	−0.57	0.42	−0.56	0.30	−0.51	−0.10	−1.10	−0.37	−0.17	−1.92	−0.92	−0.17	−1.48
cc-pVTZ	0.23	1.21	0.08	0.30	−0.76	−0.10	−1.68	−0.51	0.96	−1.28	0.08	−0.43	−1.01
aug-cc-pVTZ	−0.55	−0.18	−0.58	0.07	−0.57	−0.32	−1.17	−0.41	0.06	−2.11	−0.84	−0.30	−2.02

[a] A negative sign means that the theoretical value is less than the experimental frequency.

TABLE 11: Percentage Errors for Theoretical Harmonic Vibrational Frequencies for C_2H_2, HCN, and SiH_4[a]

	C_2H_2					HCN			SiH_4			
level of theory	ω_1	ω_2	ω_3	ω_4	ω_5	ω_1	ω_2	ω_3	ω_1	ω_2	ω_3	ω_4
SCF												
TZ3P(2f,2d)	4.92	10.1	3.92	30.3	16.3	4.88	13.1	20.9	3.04	8.65	2.16	8.72
TZ3P(2f,2d)+2diff	4.92	10.0	3.89	30.3	16.3	4.85	13.0	20.9	3.00	8.75	2.16	8.72
cc-pVTZ	5.12	10.2	4.13	29.3	16.2	5.14	13.1	20.5	2.69	8.54	1.98	8.40
aug-cc-pVTZ	5.12	10.1	4.07	29.8	16.3	5.02	13.0	20.8	2.69	8.54	2.02	8.29
MP2												
6-311G(3d,3p)	1.52	−2.24	1.26	−15.3	2.41	0.55	−5.36	−2.75	1.59	4.90	1.50	2.91
6-311++G(3d,3p)	0.72	−2.74	0.47	−23.1	−0.94	0.35	−5.50	−2.20	1.54	5.00	1.50	2.91
cc-pVTZ	1.34	−1.59	0.94	−5.61	0.80	0.99	−4.79	−1.10	1.23	4.58	1.32	2.37
aug-cc-pVTZ	1.12	−1.99	0.50	−3.69	0.94	0.73	−5.03	−1.24	1.10	4.37	1.14	1.94
CISD												
TZ3P(2f,2d)	2.26	4.58	1.26	4.65	5.76	2.21	5.50	7.57	1.01	4.27	0.84	2.80
TZ3P(2f,2d)+2diff	2.26	4.58	1.23	2.72	5.89	2.12	5.50	7.84	1.01	4.17	0.84	2.69
cc-pVTZ	2.66	4.73	1.87	7.53	6.56	2.53	5.45	6.88	0.62	4.17	0.57	2.37
aug-cc-pVTZ	2.52	4.53	1.52	9.29	6.83	2.32	5.35	7.29	0.57	3.96	0.44	1.94
CCD												
6-311G(3d,3p)	0.63	1.69	0.03	−15.4	2.41	0.58	2.30	0.41	0.22	3.54	0.13	1.94
6-311++G(3d,3p)	0.54	1.34	−0.06	−16.8	1.34	0.46	2.16	0.96	1.54	5.00	1.50	2.91
cc-pVTZ	2.66	4.73	1.87	1.60	3.48	1.13	3.10	2.89	1.23	4.58	1.32	2.37
aug-cc-pVTZ	1.17	2.49	0.15	3.53	3.61	0.87	2.96	3.16	1.10	4.38	1.14	1.94
QCISD												
6-311G(3d,3p)	0.34	0.55	−0.15	−17.3	1.47	0.17	0.80	−0.69	0.0	3.31	−0.13	1.51
6-311++G(3d,3p)	0.26	0.20	−0.23	−18.7	0.40	0.06	0.61	−0.28	−0.04	3.33	−0.18	1.51
cc-pVTZ	1.09	1.59	0.41	−1.12	2.54	0.06	1.55	1.93	−0.40	3.02	−0.35	0.97
aug-cc-pVTZ	0.92	1.34	0.03	0.96	2.81	0.49	1.46	2.06				
CCSD												
TZ3P(2f,2d)	0.69	1.89	−0.23	−3.53	1.87	0.49	2.21	2.61	0.04	3.12	−0.04	1.40
TZ3P(2f,2d)+2diff	0.69	1.84	−0.23	−5.77	1.87	0.41	2.21	2.89	0.04	3.12	−0.04	1.40
cc-pVTZ	1.17	1.99	0.44	−0.32	2.68	0.87	2.16	2.06	−0.35	3.02	−0.31	1.08
aug-cc-pVTZ	0.97	1.79	0.06	1.60	3.08	0.60	2.07	2.34	−0.44	2.81	−0.48	0.65
CCSD(T)												
TZ3P(2f,2d)	−0.08	−0.50	−0.88	−11.2	−1.07	−0.38	−0.85	−1.10	−0.35	2.50	−0.40	0.43
TZ3P(2f,2d)+2diff	−0.08	−0.55	−0.91	−14.1	−0.94	−0.47	−0.85	−0.83	−0.35	2.50	−0.40	0.43
cc-pVTZ	0.46	−0.35	−0.15	−7.37	−0.13	0.06	−0.85	−1.51	−0.97	2.50	−0.66	0.22
aug-cc-pVTZ	0.23	−0.65	−0.70	−4.97	0.13	−0.26	−0.99	−1.38	−0.88	2.19	−0.79	−0.43

[a] A negative sign means that the theoretical value is less than the experimental frequency.

that the best overall accord between theoretical and experimental IR intensities is obtained from computations employing the Dunning correlation consistent types of basis sets. The consistency between theoretical and experimental intensity values is

TABLE 12: Average Percentage Errors For Theoretical Infrared Intensities

level of theory	H_2O	CH_4	H_2CO	HCCH	HCN[a]	SiH_4
SCF						
cc-pVTZ	168.3	37.4	84.8	29.8	24.1	60.4
aug-cc-pVTZ	190.3	35.1	109.1	31.8	27.8	57.2
MP2						
cc-pVTZ	39.7	25.8	22.2	18.7	30.1	25.1
aug-cc-pVTZ	58.0	21.1	7.8	18.6	34.5	24.2
CISD						
cc-pVTZ	46.0	5.0	30.6	17.8	23.6	25.5
aug-cc-pVTZ	64.7	2.5	21.4	17.8	26.1	23.6
CCD						
cc-pVTZ	30.5	8.7	25.2	12.4	37.8	25.1
aug-cc-pVTZ	51.9	6.5	14.9	12.3	39.8	24.2
QCISD						
cc-pVTZ	15.0	3.1	23.0	11.6	16.9	15.1
aug-cc-pVTZ	28.0	2.1	11.9	11.6	21.0	–
CCSD						
cc-pVTZ	18.1	3.8	23.7	11.5	20.2	19.9
aug-cc-pVTZ	34.9	2.3	11.3	11.4	23.0	18.1
CCSD(T)						
cc-pVTZ	6.3	5.0	21.1	26.0	15.6	15.1
aug-cc-pVTZ	14.3	3.7	7.3	8.7	14.8	13.8

[a] Because of the very low experimental value for I_2 of HCN (≤ 0.1 km mol^{-1}) this intensity value is not considered.

clearly improved when applying the larger Dunning sets. As already shown, for the other molecular properties studied, the aug-cc-pVTZ computations, which are available for all molecules, clearly produced more accurate theoretical estimates.

The effect of inclusion of diffuse functions on the accuracy of IR intensity predictions is not always clearly expressed. For QCISD computations in the cases of H_2O and HCN the inclusion of diffuse functions in going from cc-pVTZ to aug-cc-pVTZ basis sets does not lead to better accord between theory and experiment. Overall, the quality of theoretical predictions by the two basis sets is quite similar. For H_2CO, however, the aug-cc-pVTZ QCISD results are much superior than these employing the cc-pVTZ basis set (Tables 3). For CCSD(T) computations, again, the inclusion of diffuse functions improves the results for the IR intensities of the H_2CO molecule. The formaldehyde computations employing the aug-cc-pVTZ basis set are far superior to the cc-pVTZ results.

The results show that quantitative IR intensity predictions may be obtained from computations employing the CCSD(T) method combined with the Dunning correlation consistent triple-ζ basis sets. The inclusion of diffuse functions appears to be quite essential. Quite satisfactory results, considering the experimental errors, are also obtained from the CCSD and QCISD methods.

IV. Conclusions

The systematic study of the accuracy of theoretical predictions at seven different levels of ab initio molecular orbital theory shows that current quantum mechanical methods are able to predict a number of molecular properties with accuracy falling often within the limits of experimental errors. Correlated levels of theory, MP2, CISD, CCD, QCISD, CCSD, and CCSD(T), combined with extended basis sets are needed to arrive at satisfactory estimates for the equilibrium geometry, dipole moment and harmonic vibrational frequencies. The Dunning correlation consistent type triple-ζ or higher basis sets usually produce plausible accord between theory and experiment for these quantities. Our best global accord is obtained from the CCSD(T) levels of theory employing Dunning's triple-ζ sets including diffuse functions.

Quantitative accord for infrared intensities between theoretical predictions and experimentally determined values is achieved at the QCISD, CCSD, and CCSD(T) levels of theory employing Dunning's aug-cc-pVTZ type of basis set. The best overall agreement for the infrared intensities is achieved at the aug-cc-pVTZ CCSD(T) level of theory, with an average accuracy for all vibrations in a molecule ranging from 3.7 to 14.8% and maximum deviations for particular modes not exceeding 26%. As we have discussed, some of these deviations are likely due to experimental limitations.

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