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Density functional theory and post-Hartree-Fock studies on molecular structure and harmonic vibrational spectrum of formaldehyde

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Abstract. Density functional theory (DFT) with the Becke's three-parameter exchange correlation functional and the functional of Lee, Yang and Parr, gradient-corrected functionals of Perdew, and Perdew and Wang [the DFT(B3LYP), DFT(B3P86) and DFT(B3PW91) methods, respectively], and several levels of conventional ab initio post-Hartree-Fock theory (second- and fourth-order perturbation theory Møller-Plesset MP2 and MP4(SDTQ), coupled cluster with the single and double excitations (CCSD), and CCSD with perturbative triple excitation [CCSD(T)], configuration interaction with the single and double excitations [CISD], and quadratic configuration interaction method [QCISD(T)], using several basis sets [ranging from a simple 6-31G(d,p) basis set to a 6-311++G(3df, 2pd) one], were applied to study of the molecular structure (geometrical parameters, rotational constants, dipole moment) and harmonized infrared (IR) spectrum of formaldehyde (CH_2O). High-level ab initio methods CCSD(T) and QCISD(T) with the 6-311++G(3df, 2pd) predict correctly molecular parameters, vibrational harmonic wavenumbers and the shifts of the harmonic IR spectrum of $^{12}CH_2{}^{16}O$ upon isotopic substitution.

Key words: Density functional theory – Post-Hartree-Fock – Formaldehyde – Structure – IR spectrum

1 Introduction

Accurate vibrational force constants remain as largely unachieved goals of molecular spectroscopy. Despite immense efforts in detailed vibrational analysis of infrared (IR), Raman, and results of spectroscopic experiments using a sophisticated laser equipment that have gone into achieving this goal, few molecules have their harmonic force field known to the sufficiently high force-constant accuracy necessary as a starting point for theoretical calculations: e.g., for description of dynamic processes. Such a force constant accuracy requirement corresponds, in general, to less than 1% of frequency accuracy, i.e., less than 10 cm^{-1} on the average. Even for a small molecule possessing high symmetry, such as formaldehyde (CH_2O), the harmonic frequencies or harmonic force fields are difficult to obtain. The main reason is that secure anharmonic corrections to fundamental frequencies are not easily acquired.

Formaldehyde is a parent compound for many important species possessing a carbonyl group. Due to the small size of this model system, it has been used to check the reliability of quantum-mechanical calculating methods. It is also probably the most extensively studied nonlinear tetratomic molecule, as far as vibrational spectroscopy is concerned [1, 2]. However, detailed examination of the IR spectra of formaldehyde and its isotopic derivatives lead to an estimates of harmonized vibrational frequencies, analysis of Coriolis resonances and strong Fermi resonance between fundamental and combination modes, etc. shows that they are incomplete. Particular, sets of harmonic frequencies obtained from the experimental or empirical (adjusted) estimates differ substantially from each other. Although important efforts, both experimental and computational, have recently been undertaken concern to vibrational states (Refs. [3–19]), there remains uncertainty, and all the harmonic frequencies still cannot be regarded as definitive. Nevertheless, formaldehyde is an important molecule for calibrating theoretical harmonic force fields methods and for refining our understanding of the structure-spectroscopic property relationship.

It is worth reviewing briefly the history of theoretical attempts to calculate harmonic force fields for small molecules. Early conventional ab initio efforts at the Hartree-Fock (HF) level led to about 10% discrepancies (10 cm^{-1}) between predicted and observed fre-

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quencies, even for modes that are thought to be quite harmonic. The post-HF methods, including the Møller-Plesset perturbation techniques, single- and multireference configuration interaction (CISD and MRCI), and coupled-cluster approaches [CCSD and CCSD(T)] as applied to predict force fields, share several limitations, namely the use of a basis set of limited size, and the numbers of occupied and virtual orbitals for description of electron correlation. Most calculations have been limited to second-order perturbation theory (MP2), despite the fact that this approach is known to have serious deficiencies for multiple bonds. Most calculations have been carried out using the valence double-ζ basis set [e.g., 6-31G(d,p)] or lower. In general, there are 5% (50–100 cm^{-1}, on the average) discrepancies between predicted and observed frequencies at the MP2/6-31G(d,p) level, and this is the result for formaldehyde.

In our previous papers [14, 15], we tried to remove some theoretical deficiencies in all-electron calculation within the MP2(full) approach by using a relatively large 6-311G(3df, 2p) basis set. The approximately 25 cm^{-1} average discrepancy between calculated and experimental harmonic frequencies clearly brings out the deficiency of MP2 theory for predicting vibrational frequencies, even when used with extensive basis sets. The MP2 limitation was recently taken on in a series of calculations carried out by Thomas et al. [16] within several coupled-cluster approximations. Treatments of electron correlation by the full single, double, and triple excitation coupled cluster method [CCSD(T)] give very similar predictions to those obtained by highly accurate, computationally expensive multireference configuration interaction with single and double excitations (MRCISD). However, Thomas et al. [16] employed a relatively modest basis set, namely the standard Huzinaga-Dunning double-ζ plus polarization functions. Again, the average disparity between the best calculated and experimental frequencies exceeded 20 cm^{-1}. Very recently, Billes [18] presented a systematic study on the basis-set dependence of the harmonic force field and harmonic frequencies of formaldehyde within the HF, MP2 and CIS methods, and De Proft et al. [19] applied the DFT(B3LYP) method with correlation-consistent polarized valence double- and triple-ζ basis sets (cc-pVDZ, cc-pVTZ) and QCISD approach with cc-pVTZ to predict harmonic frequencies and intensities of a several small molecules, including formaldehyde. We will return to these results later, when discussing our predictions.

The aim of the present paper is to report the results of calculations carried out utilizing a large saturated by polarization and diffusive functions basis sets at theoretical levels that are appropriate for recovering a large fraction of the correlation energy. These include MP4(SDTQ) and CCSD calculations, along with its extension to include perturbative estimates of the connected triple excitations [CCSD(T)], using the basis sets 6-311G(3df, 2p) and 6-311++G(3df, 2p). The 6-311G(3df, 2pd) and 6-311++G(3df, 2pd) basis sets were also used in the QCISD(T) calculations. For the sake of comparison, we have also carried out density functional theory (DFT) calculations. This method is developing rapidly as a cost-effective general approach for studying physical properties of molecules using techniques similar to conventional HF theory, with the additional feature that a description of electron correlation is included. In this paper, we report the application of the DFT method with the three hybrid exchange-correlation functionals B3LYP, B3P86, and B3PW91, using several basis sets [starting from 6-31G(d,p) to 6-311++G(3df, 2pd)] for prediction of the molecular parameters and vibrational IR spectrum (and harmonic force field) of formaldehyde.

We have two principal reasons for computing an accurate harmonic force field for formaldehyde. First, it serves as input into dynamic studies of overtone spectrum and intramolecular energy transfer in a molecule that serves as a model for many chemically and biologically important species. Second, it is important to establish an adequate theory level for ab initio calculation of harmonic force field with CCSD-, MP4(SDTQ)-, and MP2-level calculations using the valence triple-ζ basis set augmented by polarization and diffusive functions. This comparison serves to quantify the importance of higher-order electron correlation contributions to vibrational force fields. The upshot of the present study will be, as postulated previously by Lee and Scuseria [20], that the errors in the CCSD(T) predicted harmonic frequencies fall within the 10 cm^{-1} window and thus CCSD(T) and/or QCISD(T) methods, *when employed with an adequate basis set*, are essential for spectroscopically useful predictions.

2 Computational methods

Two quantum-mechanical approaches were used in this study: (a) DFT [21–24] with the hybrid functionals: Becke's three-parameter exchange correlation functional [25–27] and the correlation functional of Lee et al. [28], gradient-corrected functionals of Perdew [29], and Perdew and Wang [30] [the DFT(B3LYP), DFT(B3P86) and DFT(B3PW91) methods, respectively], and (b) conventional ab initio post-HF methods: second- and four-order perturbation theory Møller-Plesset (MP2, MP4(SDTQ)) [31, 32], coupled-cluster with the single and double substitutions from HF reference determinant (CCSD) [33–37], and CCSD with the perturbative triple excitations (CCSD(T)) [38], configuration interaction with the single and double substitution from the HF determinant (CISD) [39–41], and quadratic configuration CI method (QCISD(T)) [42–44]. The calculations were carried out using standard basis sets ranging from 6-31G(d,p) to 6-311++G(3df, 2pd) [32]. The optimizations of molecular geometry of formaldehyde and harmonic vibrational calculations were carried out within the C_{2v} symmetry. All quantum-mechanical calculations were performed with the GAUSSIAN 92 and 94 programs [45]. The symmetrized vibrational force constant matrix elements for formaldehyde were calculated using the PACK program [46]. The same program was used to predict the IR spectra of deuterated formaldehyde using the force constant matrix from the corresponding ab initio or DFT calculations for formaldehyde itself.

3 Results and discussion

3.1 Molecular parameters

The experimental gas-phase geometry, rotational constants and dipole moment are well-known for formaldehyde. These parameters are presented in Tables 1–3, together with the predicted ones calculated by different approaches. It is seen from Table 1 that DFT calculations fail in the prediction of the HCH bond angle of the molecule when using small basis sets without diffusive functions, giving a value about 1° smaller than experimental ones. On the other hand, when adding diffusive functions to small basis sets, the predicted HCH bond angle is increased by about 0.5–1.0°. The value of the dipole moment is also increased when diffusive functions are added to small basis sets. The best agreement between experimental and predicted molecular parameters is when a large basis set [6-311++G(3df, 2pd)] is used in DFT calculations. However, different functionals give similar final results.

As to the results of the conventional MP2 calculations, the predicted molecular parameters at both the MP2(full) and MP2(fc) levels are in fact the same when using the specific basis sets. However, the predicted parameters depend strongly on the quality of the basis set. It seems that the best agreement of the predicted parameters with the experimental data is for the MP2 calculation with the 6-311G(3df, 2pd) basis set. The MP2 calculation with the extended 6-311G(3df, 2pd) basis set by inclusion of diffusive functions on all atoms gives molecular parameters that are slightly worse. It is interesting that the high-electron-correlated method QCISD(T) with the 6-311G(3df, 2pd) basis set also gives parameters in better agreement with the experimental data when comparing the results of the QCISD(T)/6-311++G(3df, 2pd) calculations (Table 3).

3.2 Vibrational spectrum

The vibrational IR spectrum of formaldehyde ($^{12}CH_2{}^{16}O$) and its several isotopic species have been measured by a number of groups and analyzed in several studies (for review on spectroscopy of CH_2O molecule see Refs [1, 2]. However, there is still interest in refining our understanding of the structure-spectroscopic relationship for this model species. Though both the Coriolis and Fermi resonances make somewhat fruitlessly second-order perturbation theory-type expansions of the vibrational levels to estimate vibrational constants and harmonized vibrational frequencies, several attempts have been undertaken recently to determine the harmonic wavenumbers for CH_2O.

Table 1. DFT optimized geometrical parameters (bond distances r in angstroms, bond angles ∡ in degrees), rotational constants A, B, and C (in megahertz, dipole moments μ in debyes) of formaldehyde. Experimental data[a]

	r(CO)	r(CH)	∡(HCH)	A	B	C	μ
B3LYP							
6-31G(d,p)	1.2067	1.1105	115.22	285167	38625	34018	2.183
6-31++G(d,p)	1.2096	1.1085	116.24	283014	38594	33962	2.495
6-311G(d,p)	1.1999	1.1049	115.48	284594	39047	34336	2.240
6-311++G(d,p)	1.2018	1.1082	115.99	283891	39016	34301	2.460
6-311G(2d,2p)	1.1985	1.1070	115.68	285465	39176	34448	2.216
6-311G(3df,2p)	1.1966	1.1071	115.81	285007	39302	34539	2.203
6-311G(3df,2pd)	1.1965	1.1068	115.82	285136	39311	34548	2.205
6-311++G(3df,2pd)	1.1985	1.1060	116.06	284830	39228	34479	2.399
B3P86							
6-31G(d,p)	1.2042	1.1100	115.31	285144	38782	34138	2.218
6-31++G(d,p)	1.2064	1.1081	116.24	283175	38776	34106	2.480
6-311G(d,p)	1.1977	1.1097	115.59	284370	39192	34445	2.270
6-311++G(d,p)	1.1989	1.1084	116.00	283767	39178	34425	2.446
6-311G(2d,2p)	1.1964	1.1072	115.83	284923	39313	34546	2.241
6-311G(3df,2p)	1.1965	1.1075	115.89	284600	39431	34633	2.218
6-311G(3df,2pd)	1.1965	1.1072	115.90	284715	39438	34640	2.220
6-311++G(3df,2pd)	1.1959	1.1065	116.09	284468	39381	34592	2.380
B3PW91							
6-31G(d,p)	1.2048	1.1107	115.26	284893	38735	34009	2.208
6-31++G(d,p)	1.2068	1.1089	116.18	282952	38742	34076	2.469
6-311G(d,p)	1.1983	1.1107	115.24	284075	39143	34403	2.254
6-311++G(d,p)	1.1996	1.1094	115.95	283436	39129	34382	2.433
6-311G(2d,2p)	1.1970	1.1084	115.76	284530	39260	34500	2.223
6-311G(3df,2p)	1.1951	1.1086	115.82	284238	39377	34586	2.203
6-311G(3df,3pd)	1.1951	1.1083	115.83	284340	39384	34593	2.204
6-311++G(3df,2pd)	1.1966	1.1076	116.03	284092	39325	34544	2.368
Experimental	1.206	1.108	116.6	281970.57	38836.05	34002.20	2.33168
	1.203	1.099	116.5				
	1.2033	1.1005	116.30				

[a] Experimental geometries taken from Refs. [48–50], respectively; experimental rotational constants taken from Ref. [51]; experimental dipole moment from Ref. [52]

Table 2. MP2(full) and MP2(fc) optimized geometrical parameters (bond distances r in angstroms, bond angles $\measuredangle$ in degrees), rotational constants A, B, and C (in megahertz; dipole moments μ in debyes) of formaldehyde. Experimental data[a]

	r(CO)	r(CH)	$\measuredangle$(HCH)	A	B	C	μ
6-31G(d,p)							
full	1.2194	1.0993	115.53	289955	38026	33617	2.229
fc	1.2203	1.1004	115.52	289425	37965	33563	2.231
6-31++G(d,p)							
fc	1.2242	1.0986	116.51	287267	37874	33462	2.520
6-311G(d,p)							
full	1.2100	1.1055	115.70	286195	38527	33956	2.171
fc	1.2106	1.1060	115.67	286028	38487	33923	2.171
6-311++G(d,p)							
fc	1.2130	1.1048	116.15	285158	38415	33854	2.391
6-311G(2d, 2p)							
full	1.2091	1.0986	116.07	288661	38672	34103	2.204
fc	1.2103	1.0997	116.08	288019	38601	34039	2.205
6-311G(3df, 2p)							
full	1.2046	1.0977	116.23	287575	38944	34299	2.208
fc	1.2066	1.1014	116.26	286588	38821	34190	2.210
6-311++G(3df, 2p)							
fc	1.2089	1.1004	116.53	286263	38726	34201	2.202
6-311G(3df, 2pd)							
fc	1.2065	1.1010	116.29	286707	38833	34111	2.404
6-311++G(3df, 2pd)							
fc	1.2089	1.1004	116.54	286251	387267	34112	2.395
Experimental	1.206	1.108	116.6	281970.57	38836.05	34002.20	2.33168
	1.203	1.099	116.5				
	1.2033	1.005	116.30				

[a] For the references for experimental data see footnote to Table 1

Table 3. Geometries (bond distances r in angstroms, bond angles $\measuredangle$ in degrees) and rotational constants A, B, and C (in megahertz, dipole moments μ in debyes) calculated at the ab initio high electron-correlated levels (frozen-core approximation) for formaldehyde. Experimental data[a]

Method, basis set	r(CO)	r(CH)	$\measuredangle$(HCH)	A	B	C
CISD						
6-311G(3df, 2p)	1.1922	1.0973	116.20	288914	39686	34893
6-311++G(3df, 2p)	1.1932	1.0972	116.27	288735	39634	34850
CCSD						
6-311G(3df, 2p)	1.1995	1.1021	116.23	286272	39221	34495
6-311++G(3df, 2p)	1.2011	1.1017	116.40	285966	39149	34435
MP4(SDTQ)						
6-311G(3df, 2p)	1.2107	1.1056	116.12	284800	38535	33942
6-311++G(3df, 2pd)	1.2131	1.1048	116.40	284385	38439	33862
CCSD(T)						
6-311G(3df, 2p)	1.2062	1.1045	116.28	284885	38820	34164
6-311++G(3df, 2pd)	1.2080	1.1037	116.50	284675	38750	34108
QCISD(T)						
6-311G(3df, 2pd)	1.2065	1.1043	116.28	285049	38806	34156
6-311++G(3df, 2pd)	1.2082	1.1040	116.45	284646	38730	34091
Experimental	1.206	1.108	116.6	281970.57	38836.05	34002.20
	1.203	1.099	116.5			
	1.2033	1.1005	116.30			

[a] For the references for experimental data see footnote to Table 1

Reisner et al. [3], using the stimulated emission pumping technique, determined the set of normal mode vibrational constants and harmonic frequencies with high precision. Later, Wohar and Jagodzinski [5] presented the accurate experimental IR spectra of ^{13}C isotopic species of formaldehyde ($^{13}\mathrm{CH}_2{}^{16}\mathrm{O}$, $^{13}\mathrm{CD}_2{}^{16}\mathrm{O}$), and also determined their harmonic wavenumbers and general harmonic force field. Martin et al. [17] calculated a quartic force field using CCSD(T) method with a large basis set and adjusted harmonic frequencies. Very recently Bouwens et al. [6], using dispersed fluorescence spectroscopy, significantly extended the last experiment, assigning several new states. Burleigh et al. [7] have calculated a quartic force field for formaldehyde, refining the ab initio quartic force field of Martin et al. [17] by iteratively fitting a subset of the coefficient of a Taylor-series expansion of the potential-energy surface to observed transition frequencies (among them many of the states by Bouwens et al. [6]).

It is important to note a few other attempts to obtain the quartic force field for formaldehyde, providing information on harmonic frequencies for this species. The first attempt was made by Harding and Ermler [12], who fitted a quartic force field to energies calculated at the CISD level using the DZP basis set. Later Clabo et al. [13], combining the CISD frequencies with an SCF anharmonic force field, predicted similar spectroscopic constants to those of Harding and Ermler. The harmonic wavenumbers from these studies and the fundamental wavenumbers from a few experimental papers are presented in Table 4.

The DFT calculations predict the harmonic ν_4 wavenumber associated with the out-of-plane bending of the molecule to be about 1200 cm^{-1} (exp. $\sim$1190 cm^{-1}). As we can see from Table 5, the predicted ν_4 wavenumber does not depend either on the functional used in DFT calculations or on the basis set. Similarly, the predicted ν_2, ν_3, and ν_6 wavenumbers (associated with the C=O stretching, CH_2 bending, and CH_2 rocking modes, respectively) do not depend strongly on the level of the DFT calculations [particularly when using the 6-311G(d,p) and better basis sets]. On the other hand, the predicted ν_1 and ν_5 wavenumbers (associated with the CH_2 symmetric and asymmetric stretchings modes, respectively) are more sensitive at the level of DFT calculations than the other wavenumbers. The characteristic features of the ν_1 and ν_5 wavenumbers predicted by the DFT approaches are their lower values (by $\sim$60–70 cm^{-1}) compared to corresponding experimental harmonic wavenumbers.

The dependence of the predicted wavenumbers on the level of conventional ab initio calculations (Table 6) is quite different compared with the data presented in Table 5 (DFT calculations). The ν_1 and ν_5 wavenumbers predicted at the high electron-correlated levels of calculations (CCSD(T), QCISD(T)) are only $\sim$5–10 cm^{-1} lower than the corresponding experimental harmonic wavenumbers. The other predicted wavenumbers are higher than the corresponding experimental harmonic wavenumbers by $\sim$2–5 cm^{-1}. In our previous MP2(full)/6-311G(3df,2p) calculations [14, 15], the predicted ν_1 and ν_5 harmonic wavenumbers were higher than experimental wavenumbers by about 40 cm^{-1}, and the wavenumbers of the remaining modes were higher by only about 10–20 cm^{-1}. Note the very good agreement between the predicted and measured absolute intensities of the vibrational modes of formaldehyde [47].

The calculated shifts of the harmonic wavenumbers of $^{12}CH_2{}^{16}O$ and $^{13}CH_2{}^{16}O$ upon deuteration (Table 7) agree with the corresponding experimental shifts to within 8 cm^{-1}, except the shifts of the ν_3 mode (CH_2 bending) that are predicted to be at wavenumbers shorter by 13–14 cm^{-1}. The observed shifts caused by the $^{12}C \rightarrow {}^{13}C$ substitution are not higher than 40 cm^{-1}, and the predicted shifts agree with the experimental data to within 1–2 cm^{-1}. The harmonized IR spectra of the $^{12}CH_2{}^{18}O$ and $^{12}CD_2{}^{18}O$ species are still elusive. We expect the same agreement as above for the predicted shifts of the harmonic wavenumbers of $^{12}CH_2{}^{16}O$ upon ^{18}O substitution (within 1–2 cm^{-1}) and those of $^{12}CH_2{}^{18}O$ upon dideuteration (Table 7).

In summary, the applied high electron-correlated levels of ab initio calculations CCSD(T) and/or QCISD(T) allow for an accurate prediction of the molecular parameters and harmonic vibrational IR spectrum of formaldehyde, as well as the shifts of the IR spectrum caused by isotopic substitution. The DFT approach with the large extended basis set does not improve much the final results for molecular parameters and harmonic IR spectrum of formaldehyde compared to the results of the DFT calculations with a simple basis set.

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Table 4. Experimental harmonic and fundamental vibrational frequencies (cm^{-1}), and absolute intensities (km/mol) for formaldehyde

Mode[a]		Harmonic frequencies							Fundamental frequencies			Absolute intensities
		[6][b]	[7][c]	[17][d]	[3][e]	[52, 5]	[53]	[12][f]	[6]	[3]	[4]	[54]
A_1	ν_1	2953	2932	2923	2978	2944	2944	2937	2837	2811	2808	75.5 ± 7.05
	ν_2	1779	1777	1778	1778	1764	1761	1778	1753	1756	1759	73.99 ± 5.29
	ν_3	1540	1535	1539	1529	1563	1517	1554	1497	1500	1508	11.15 ± 1.02
B_1	ν_4	1185	1188	1194	1191	1191	1187	1188	1172	1170	1175	6.49 ± 0.64
B_2	ν_5	2933	3007	2999	2997	3009	3033	3012	2845	2861	2829	87.6 ± 8.02
	ν_6	1282	1272	1276	1299	1288	1282	1269	1255	1251	1256	9.94 ± 0.97

[a] The modes are given in the standard spectroscopic order [the molecule of C_{2v} symmetry is oriented in the (y,z) plane with the z axis along the C=O bond]: ν_1 – CH_2 symmetric stretching, ν_2 – C=O stretching, ν_3 – CH_2 bending, ν_4 – out-of-plane bending, ν_5 – CH_2 asymmetric stretching, ν_6 – CH_2 rocking

[b] Harmonic frequencies quoted in Ref. [7]

[c] Based in iteratively fitting of the potential-energy surface (ab initio CCSD(T) quartic force field calculations [7]) to observed transition frequencies [4, 6]

[d] Adjusted values [based on CCSD(T) calculations]

[e] Experimental values from stimulated emission pumping spectra

[f] Empirical (adjusted) harmonic frequencies (based on quartic force field fitted to energies calculated at the CISD level with DZP basis set)

Table 5. Predicted harmonic IR spectrum (frequency ν in cm^{-1}, absolute intensity A in km/mol) of formaldehyde at the DFT levels. For experimental data see Table 4

Method, mode		Basis set:															
		6-31G(d,p)		6-31++G(d,p)		6-311G(d,p)		6-311++G(d,p)		6-311G(2d,2p)		6-311G(3df,2p)		6-311G(3df,2pd)		6-311++G(3df,2pd)	
		ν	A	ν	A	ν	A	ν	A	ν	A	ν	A	ν	A	ν	A
DFT(B3LYP)																	
A_1	ν_1	2897	55	2912	67	2868	65	2883	72	2876	67	2871	68	2874	67	2883	73
	ν_2	1846	97	1819	117	1827	111	1814	123	1825	101	1835	98	1835	98	1821	114
	ν_3	1555	7	1538	7	1539	8	1531	9	1538	10	1536	11	1536	11	1533	11
B_1	ν_4	1200	2	1197	4	1202	3	1202	5	1199	3	1201	6	1202	6	1201	5
B_2	ν_5	2954	159	2977	131	2917	170	2941	136	2927	148	2920	129	2926	129	2940	118
	ν_6	1274	13	1262	10	1270	15	1260	9	1272	13	1269	14	1269	14	1266	11
DFT(B3P86)																	
A_1	ν_1	2910	56	2925	68	2885	64	2897	71	2891	65	2885	67	2888	66	2895	72
	ν_2	1863	99	1841	117	1846	112	1837	123	1843	102	1852	99	1852	99	1842	113
	ν_3	1552	6	1537	6	1537	8	1530	8	1534	9	1531	11	1532	11	1529	10
B_1	ν_4	1200	2	1199	4	1203	3	1203	5	1199	4	1200	7	1201	7	1201	6
B_2	ν_5	2968	159	2991	131	2939	159	2957	132	2946	138	2938	122	2943	122	2954	114
	ν_6	1273	12	1262	9	1270	14	1260	9	1270	13	1267	13	1267	13	1264	11
DFT(B3PW91)																	
A_1	ν_1	2910	57	2920	69	2879	65	2891	73	2883	66	2878	68	2881	68	2888	74
	ν_2	1863	99	1839	117	1844	112	1834	123	1840	102	1849	99	1849	99	1838	113
	ν_3	1552	6	1537	6	1537	7	1529	8	1533	9	1530	11	1530	11	1528	10
B_1	ν_4	1200	2	1198	5	1202	3	1203	5	1198	3	1199	6	1200	6	1200	6
B_2	ν_5	2968	161	2985	134	2931	164	2950	136	2936	142	2929	127	2934	126	2946	118
	ν_6	1273	12	1262	9	1269	14	1259	9	1269	13	1266	13	1266	13	1263	11

Table 6. Predicted harmonic frequencies (in cm^{-1}) of formaldehyde at the ab initio electron-correlated levels (frozen-core approximation)[a]

Mode		HF		MP2		CISD		CCSD		MP4		CCSD(T)		QCISD(T)		
		a	b++	a	b++	a	a++	a	a++	a	b++	a	b++	a	b	b++
A_1	ν_1	3081	2068	2968	2970	3016	3019	2957	2962	2916	2916	2925	2926	2927	2919	2922
	ν_2	2009	1999	1784	1769	1895	1888	1841	1831	1754	1738	1790	1779	1788	1787	1777
	ν_3	1652	1650	1552	1547	1588	1586	1558	1556	1530	1524	1541	1536	1539	1537	1535
B_1	ν_4	1338	1338	1204	1202	1248	1248	1210	1209	1182	1180	1187	1185	1185	1186	1185
B_2	ν_5	3146	3154	3039	3048	3084	3023	3023	3032	2978	2985	2990	2997	2991	2985	2992
	ν_6	1372	1369	1279	1274	1314	1311	1289	1286	1264	1257	1273	1267	1271	1268	1266

[a] For experimental frequencies and notation see Table 4. Abbreviations for the basis sets: a, 6-311G(3df,2p); a++, 6–311++G(3df,2p); b, 6-311G(3df,2pd); b++, 6-311++G(3df, 2pd)

Table 7. Calculated and experimental shifts of harmonic wavenumbers and experimental shifts of wavenumbers of fundamentals (in cm^{-1}) of $^{12}CH_2{}^{16}O$ upon isotopic substitution[a]

Mode		$^{12}CH_2{}^{16}O \rightarrow {}^{12}CD_2O$			$^{12}CH_2{}^{16}O \rightarrow {}^{13}CH_2O$			$^{13}CH_2{}^{16}O \rightarrow {}^{13}CD_2O$			$^{12}CH_2{}^{16}O \rightarrow {}^{12}CH_2{}^{18}O$			$^{12}CH_2{}^{18}O \rightarrow {}^{12}CD_2{}^{18}O$		
		Calculated		Observed	Calculated		Observed	Calculated		Observed	Calculated		Observed	Calculated		Observed
		CCSD(T)	QCISD(T)		CCSD(T)	QCISD(T)		CCSD(T)	QCISD(T)		CCSD(T)	QCISD(T)		CCSD(T)	QCISD(T)	
A_1	ν_1	795	794	800(725)	5	4	3(3)	804	803	811(736)	0	0	–	797	795	–
	ν_2	49	50	46(45)	39	38	39(38)	41	42	35(41)	33	33	–	89	89	–
	ν_3	415	414	425(399)	0	0	0(0)	416	415	429(399)	12	12	–	420	420	–
B_1	ν_4	236	235	238(229)	12	12	12(12)	239	239	241(232)	2	1	–	237	237	–
B_2	ν_5	759	758	754(683)	13	13	13(12)	764	763	759(687)	0	0	–	759	758	–
	ν_6	268	268	276(262)	10	9	9(9)	268	268	279(265)	6	5	–	275	274	–

[a] The shifts of the experimental harmonized wavenumbers and wavenumbers of fundamentals (in parentheses) from Ref. [5]

References

1. Moule DC, Walsh AD (1975) Chem Rev 75:67
2. Clouthier DJ, Ramsay DA (1983 Annu Rev Phys Chem 34:31
3. Reissner DE, Field RW, Kisney JL, Dai HL (1984) J Chem Phys 80:5968
4. Tipton T (1985) J Mol Spectrosc (1985) 114:239
5. Wohar MM, Jagodzinski PW (1991) J Mol Spectrosc 148:13
6. Bouwens RJ, Hammerschmidt JA, Grzeskowiak MM, Stegink TA, Yorba PM, Polik WF (1996) J Chem Phys 104:460
7. Burleigh DC, McCoy AB, Sibert III EL (1966) J Chem Phys 104:480
8. Luckhaus D, Coffey MJ, Fritz MD, Crim FF (1996) J Chem Phys 104:3472
9. Handy NC, Carter S (1981) Chem Phys Lett 79:118
10. Maessen B, Wolfsberg M (1984) J Chem Phys 80:4651
11. Maessen B, Wolfsberg M (1984) J Phys Chem 88:6420
12. Harding LB, Ermler WC (1985) J Comp Chem 6:13
13. Clabo DA, Allen WD, Remington RB, Yamaguchi Y, Schaefer III HF (1988) Chem Phys 123:187
14. Kwiatkowski JS, Leszczynski J (1992) Int J Quantum Chem: Quantum Chem Symp 26:421
15. Kwiatkowski JS, Leszczynski J (1993) J Mol Spectrosc 157:540
16. Thomas JR, DeLeeuw BJ, Vacek G, Schaefer III HF (1993) J Chem Phys 98:1336
17. Martin JML, Lee TJ, Taylor PR (1993) J Mol Spectrosc 160:105
18. Billes F (1995) J Mol Struct THEOCHEM 339:15
19. DeProft F, Martin JML, Geerlings P (1996) Chem Phys Lett 250:393
20. Lee T, Scuseria GE (1995) In: Langhoff SR (ed.) Understanding chemical reactivity. Kluver, Dordrecht, p 376
21. Hohenberg P, Kohn W (1964) Phys Rev 136:B864
22. Parr RG, Yang W (1989) Density functional theory of atoms and molecules. Oxford University Press, New York
23. Jones RO, Gunnarsson O (1989) Rev Mod Phys 61:689
24. Ziegler T (1991) Chem Rev 91:651
25. Becke AD (1988) Phys Rev A38:3098
26. Becke AD (1992) J Chem Phys 96:2155
27. Becke AD (1993) J Chem Phys 98:5648
28. Lee C, Yang W, Parr RG (1988) Phys Rev 37:B785
29. Perdew JP (1986) Phys Rev B33:8822
30. Perdew JP, Wang Y (1992) Phys Rev B45:13244
31. Møller-Plesset C (1934) Phys Rev 46:618
32. Hehre WJ, Radom L, Schleyer P von, Pople JA (1986) Ab initio molecular orbital theory. Wiley, New York
33. Bartlett RJ (1989) J Phys Chem 93:1697
34. Purvis GD, Bartlett RJ (1982) J Chem Phys 76:1910
35. Scuseria GE, Scheiner AC, Lee TJ, Rice JE, Schaefer III HF (1986) J Chem Phys 86:2881
36. Scuseria GE, Jansen CL, Schaefer III HF (1988) J Chem Phys 89:7382
37. Lee TJ, Rice JE (1988) Chem Phys Lett 152:406
38. Raghavachari K, Trucks GW, Pople JA, Head-Gordon M (1989) Chem Phys Lett 157:479
39. Pople JA, Seeder R, Krishnan R (1977) Int J Quantum Chem: Quantum Chem Symp 11:149
40. Krishnan R, Schlegel HB, Pople JA (1980) J Chem Phys 72:4654
41. Raghavachari K, Pople JA (1981) Int J Quantum Chem 20:167
42. Pople JA, Head-Gordon M, Raghavachari K (1987) J Chem Phys 87:5968
43. Pople JA, Head-Gordon M, Raghavachari K (1989) J Chem Phys 90:4635
44. Raghavachari K, Head-Gordon M, Pople JA (1990) J Chem Phys 93:1486
45. Frisch MJ, Trucks GW, Schlegel HB, Gill PMW, Johnson BG, Wong MW, Foresman JB, Robb MA, Head-Gordon M, Replogle ES, Gomperts R, Andres JL, Raghavachari K,

Binkley JS, Gonzalez C, Martin RL, Fox DJ, DeFrees DJ, Baker J, Stewart JJP, Pople JA (1993) GAUSSIAN 92/DFT, revision F.2. Gaussian, Inc., Pittsburgh, Pa

46. KuBulat K (1989) Ph.D. dissertation, University of Florida; Person WB, KuBulat K (1989) (unpublished work; private information)
47. Nakanaga T, Konto S, Saeki S (1982) J Chem Phys 76:3860
48. Takagi KT, Oka T (1963) J Phys Soc Jpn 18:1174; see Harmony MD, Laurie VW, Kuczkowski RL, Schwendeman RH, Ramsay DA, Lovas WJ, Lafferty WJ, Maki AG (1978) J Phys Chem Ref Data 8:619
49. Yamada K, Nakagawa T, Kuchitsu K, Morino Y (1971) J Mol Spectrosc 38:70
50. Duncan JL (1974) Mol Phys 28:1177
51. Winnerwisser G, Cornet RA, Birss FW, Gordon RM, Ramsay DA, Till SM (1979) J Mol Spectrosc 74:327
52. Fabricant B, Krieger D, Mautner JS (1977) J Chem Phys 67:1576