

Hartree-Fock Calculation of the Harmonic Force Constants and Equilibrium Geometry of Formaldehyde

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Using the force method, complete sets of harmonic force constants have been obtained for formaldehyde from Hartree-Fock wavefunctions. The agreement with experiment is considered particularly satisfying for the off-diagonal constants. This holds not only for a near-Hartree-Fock Gaussian basis set but also for a small but polarized 7, 3/3/1 basis set. The value even of such a small calculation is underlined by frequencies calculated from force constants corrected for almost systematic errors in the diagonal constants. Experimental force fields are critically examined, and an explanation for the surprisingly large coupling between CO and CH stretching is indicated.

Key words: Force constants – Formaldehyde

1. Introduction

This work is part of a systematic investigation on the force constants of small molecules by quantum chemical methods. Near-Hartree-Fock calculations on methane [1], ammonia [2] and water [3–5] have established that force constants can be obtained with a higher accuracy from Hartree-Fock calculations than thought hitherto. It is especially significant that the accuracy of the coupling (or interaction or off-diagonal) force constants is comparable to the accuracy of the diagonal constants. Numerically reliable calculations for coupling constants have been published only recently. Hartree-Fock calculations with moderately sized basis sets on water [5], HF, NH₃, CH₄ and BH₄⁻ [6], on ethylene [7] and on ethane and acetylene [8] also show good agreement with experiment, thus proving that calculations need not be very sophisticated to get sensible force constants. E.g. in these latter calculations coupling force constants are accurate to at least ± 0.1 mdyne/Å. Even more important, all trends are correctly reproduced. The calculations thus have predictive power, even if e.g. the diagonal bending force constants are consistently overestimated by about 20% with medium-sized basis sets.

Special attention will be paid to the coupling force constants in this paper. The reason is that these quantities are much more difficult to obtain experimentally than the diagonal force constants. It is therefore in this field that *ab initio* (or even

semiempirical) calculations can most successfully complete the experimental data. By comparing calculated coupling force constants to experimental values, we were able to decide which of the two alternative force fields for ethylene, both compatible with the experimental data, is the physical solution [7]. This result was then confirmed by experiment [9].

We can expect that force fields composed of *ab initio* coupling force constants and diagonal force constants from fits of the observed vibrational frequencies, will represent an improvement over force fields based on experimental data alone, particularly for molecules with low symmetry. This would result in improved vibrational assignments and reliable frequency predictions.

Formaldehyde is the simplest oxo compound and one might expect that its force field has been established experimentally with certainty. However, McKean and Duncan [9] have shown that there are two sets of force constants (two different vibrational assignments) which are both compatible with the existing experimental data. Only very recently have Becher and Adrian [10] measured the IR spectra of H_2^{13}CO which apparently settles this problem. Even so, there remain problems in the experimental force field (see the Discussion).

The question of the vibrational assignment and force field of acetaldehyde seems now solved by Hollenstein and Günthard [11]. Acetone, however, is still an open problem [12].

2. Calculations

Calculation of the force constants and equilibrium geometries has been carried out by the force method [13]. This method made it possible to determine all 10 quadratic force constants, some even twice, from only 9 wavefunctions¹. Briefly, this method consists of calculating the exact forces (negative derivatives of the total SCF energy with respect to nuclear coordinates) directly from the SCF wavefunction. Note that the forces calculated are not identical with the Hellmann-Feynman forces. The originally calculated Cartesian forces are transformed to internal valence or symmetry coordinates; for details see Ref. [13]. The force method not only saves computer time but is also numerically accurate: in this respect the classical energy hypersurface method often fails. Numerical accuracy can be easily checked in the force method since each coupling constant F_{ij} is obtained twice: as the numerical derivative of the force in the direction of the coordinate i with respect to coordinate j or *vice versa*. The two values are obtained from separate SCF calculations but they usually differ by less than 0.001 mdyn/Å.

Force constant calculations have been carried out around the experimental, rather than the calculated equilibrium geometry, according to the suggestion of Schwendeman [14]. The experimental r_z geometry of Tagaki and Oka [15] was used: $r_z(\text{CO}) = 1.2078 \text{ \AA}$, $r_z(\text{CH}) = 1.1160 \text{ \AA}$, $\alpha_z(\text{HCH}) = 116^\circ 31'$. The finite displacements of the coordinates were chosen on the basis of previous experience, and amounted ± 0.05 bohr for the stretching and $\pm 3^\circ$ for the bending coordinates.

¹ By using symmetrically reducible displacements it would be possible to obtain all force constants from only 7 wavefunctions.

Table 1. Parameters of the basis set^a

Location and type	Exponents
Basis set A (73/3/1):	
O, <i>s</i>	(1090, 276, 70.4), 17.8, 4.51, 1.15, 0.291
O, <i>p</i>	6.89, 1.33, 0.257
C, <i>s</i>	(575, 146, 37.3), 9.42, 2.39, 0.608, 0.154
C, <i>p</i>	4.78, 0.923, 0.178
CH midpoint, <i>s</i>	0.65
CO midpoint, <i>s</i>	1.0
CO midpoint, <i>p_y</i>	0.6
Basis set B (95/4/1):	
O, <i>s</i>	(7816.54, 1175.82, 273.188), 81.17, 27.18, 9.53, 3.5, 1.1, 0.4, 0.16
O, <i>p</i>	(31.66, 7.114), 2.075, 0.645, 0.192
C, <i>s</i>	(4232.6, 634.88, 146.1), 42.5, 14.19, 5.15, 1.97, 0.496, 0.153
C, <i>p</i>	(18.16, 3.99), 1.143, 0.359, 0.115
H, <i>s</i>	16.034, 2.216, 0.545, 0.148
CH, <i>s</i> (loc at 0.6 <i>r_{CH}</i>)	0.9
CO midpoint, <i>s</i>	1.5, 0.5
CO midpoint, <i>p_y</i>	1.0, 0.33
CO midpoint, <i>p_x</i>	0.7
Basis set C (951/4/1):	
The same as set B, augmented by	
O, <i>d_{xz}</i> , <i>d_{yz}</i> ^b	0.645
C, <i>d_{xz}</i> , <i>d_{yz}</i> ^b	0.359

^a The molecule lies in the *xz* plane, the CO bond is the *z* axis. Parentheses denote a contraction, i.e. a linear combination of functions with fixed coefficients.

^b The functions on the bonding lines replace the missing *d_{z²}*

 orbitals to a large extent.

These displacements are neither too large for anharmonicity to matter nor too small for numerical inaccuracies to appear.

The calculated geometry was determined by the force relaxation method [13]. All coordinates are simultaneously optimized in this method and the true calculated geometry is sharply determined by vanishing forces on the atoms.

In order to study the influence of the basis set on the calculated force constants, three different Gaussian basis sets were chosen; their parameters are given in Table 1. Set A is our standard 73/3/1 basis set [5–8], based on the exponents of Csizmadia *et al.* [16]. Its importance lies in the fact that calculations on larger molecules are feasible with this basis set without excessive computing costs.

Set B has been obtained by the following policy: We have started with Huzinaga's 95/4 basis set [17]. Preliminary calculations have shown that the softest *s* and *p* functions on oxygen (i.e. those with the smallest exponents) are very strongly populated. One can infer that the negative charge on oxygen makes the electron cloud less dense and that softer basis functions are desirable. Therefore an additional *s* function was added and the three outermost *s* exponents were modified accordingly. Further on, the exponents of the oxygen *p* functions were multiplied (scaled) by 0.9. The hydrogen exponents were scaled by 1.2. This factor

Table 2. Comparison of energies, orbital energies and dipole moment of formaldehyde with other calculations^a

Quantity	This work			Neumann <i>et al.</i> [19]	Winter <i>et al.</i> [20]	Newton <i>et al.</i> [21]	Buenker <i>et al.</i> [22]
	A	B	C				
Basis set, uncontracted	73/3/1	95/4/1	951/4/1	1052/41	95/3	minimum Slater	105/5
Basis set, contracted	53/3/1	74/4/1	741/4/1	532/21	95/3	—	42/1
R_{CO}	2.2825	2.2825	2.22 ^b	2.2825	2.2864	2.2864	2.2864
r_{CH}	2.1090	2.1090	2.1090	2.1090	2.1164	2.1164	2.1164
α	116°31'	116°31'	116°31'	116°31'	118°	118°	118°
$E + 113.0$	- 0.66560	- 0.89973	- 0.9038 ^c	- 0.8917	- 0.8334	- 0.4496	- 0.8094
$1a_1$	-20.5923	-20.5782	-20.5781 ^d	-20.5738	-20.5906	-20.5897	-20.5788
$2a_1$	-11.3515	-11.3479	-11.3478 ^d	-11.3431	-11.3627	-11.3565	-11.3518
$3a_1$	- 1.4216	- 1.4073	- 1.4076 ^d	- 1.4038	- 1.4299	- 1.3694	- 1.4220
$4a_1$	- 0.8688	- 0.8674	- 0.8662 ^d	- 0.8646	- 0.8666	- 0.8369	- 0.8642
$1b_1$	- 0.6826	- 0.6911	- 0.6916 ^d	- 0.6893	- 0.7020	- 0.6745	- 0.6999
$5a_1$	- 0.6467	- 0.6491	- 0.6494 ^d	- 0.6506	- 0.6437	- 0.5709	- 0.6353
$1b_2$	- 0.5369	- 0.5374	- 0.5377 ^d	- 0.5341	- 0.5355	- 0.4698	- 0.5274
$2b_1$	- 0.4333	- 0.4417	- 0.4418 ^d	- 0.4402	- 0.4423	- 0.3854	- 0.4370
Dipole moment	1.119	1.138	1.117	1.110	1.193	0.983	—

^a R , r and α are the geometry parameters, E the energy. Orbital energies are denoted by the designation of the molecular orbital. Distances are given in Bohr, energies in Hartrees and dipole moments in Debyes.

^b Extrapolated equilibrium CO distance.

^c Extrapolated for $R = 2.22$ Bohr. See also Table 3.

^d Interpolated values for $R = 2.2825$ Bohr.

is not optimum with respect to energy (the optimum is about 1.3) but here again we consider it desirable to have greater flexibility in the outer part of the electron cloud. In addition to the functions centered on nuclei, our basis set contains functions centered on bonding lines. The CH bond functions had been optimized in methane [1], the CO functions were optimized in preliminary calculations.

Set C is identical with set B but it is augmented by d functions with optimized exponents on C and O.

Only the innermost functions are contracted because our experience shows that contraction in the valence shell, as used e.g. by Newton *et al.*, strongly deteriorates force constants. Obviously, orbital flexibility is vital in all force constant calculations. Contraction coefficients were taken from a single, fully uncontracted molecular calculation.

The calculations have been carried out by our program system MOLPRO. The force program uses the converged density matrix from the SCF procedure (open or closed shell), calculates the cartesian forces and transforms them to internal coordinates. Since the only input for the force program is the specification of internal coordinates, routine calculations are no more complicated than Hartree-Fock calculations only. Calculation of the exact forces requires a significant amount of computer time, usually about twice as much as the calculation of the SCF wavefunction. The gain in information and accuracy, however, outweighs this cost.

Table 3. Forces, energies and dipole moments for basis sets *B*(95/4/1) and *C*(951/4/1)^a

Geometry ^b	Force coordinate						Energy + 113.0	Dipole moment
	CO	s.CH	s.bend	as.CH	Rock	Wagging		
Basis set B:								
$R = +0.05$	-0.79316	-0.21446	-0.00518				-0.895886	1.1923
$R = -0.05$	-0.07102	-0.17217	0.01654				-0.901385	1.0819
$r_1 = r_2 = +0.05$	-0.49340	-0.36368	0.01003				-0.897316	1.1267
$r_1 = r_2 = -0.05$	-0.43385	0.00186	0.00025				-0.900576	1.1488
$\beta_1 = \beta_2 = -1.5^\circ$	-0.43620	-0.20241	0.04540				-0.899354	1.1359
$\beta_1 = \beta_2 = +1.5^\circ$	-0.48878	-0.18566	-0.03589				-0.899506	1.1398
$r_1 = 0.05,$ $r_2 = -0.05$	-0.46404	-0.18098	0.00559	-0.17928	-0.00547		-0.898965	$\mu_z = 1.1372$ $\mu_x = -0.0190$
$\beta_1 = -1.5^\circ,$ $\beta_2 = +1.5^\circ$	-0.46249	-0.19442	0.00557	0.00522	0.03359		-0.899586	$\mu_z = 1.1380$ $\mu_x = -0.0031$
$\delta = 3^\circ$	-0.46131	-0.19426	0.00514			0.02622	-0.899572	$\mu_z = 1.1380$ $\mu_y = 0.0079$
Exp. equilibrium	-0.46338	-0.19460	0.00531				-0.899730	1.1379
Calc. equilibrium	0.00047	-0.00620	-0.00107				-0.902095	1.0854
Basis set C:								
$R = +0.05$	-0.78658	-0.20461	-0.01201				-0.897551	1.1726
$R = -0.05$	-0.06355	-0.16276	0.00926				-0.902964	1.0621

^a Forces in mdyne and in mdyneÅ for the stretching and bending coordinates, resp. energies in Hartrees, dipole moments in atomic units. The molecule lies in the *xz* plane, the CO bond being the positive *z* axis. Values which vanish by symmetry are not given.

^b Displacements from the experimental equilibrium geometry, in Bohr and degrees. See text for the definition of internal coordinates.

3. Results and Discussion

The quality of our wavefunction can be judged from a comparison of our total energies, orbital energies and dipole moments with some recent calculations [18–22], shown in Table 2. Although we considered it more important to have maximum flexibility in the valence shell than to obtain minimum energy, our basis B gives lower energy than the near-Hartree-Fock calculation of Neumann and Moskowitz [19]. This seems to originate from two sources: our basis set is less contracted than that in Ref. [19], and our basis contains functions centered between atoms. Calculation C gives the lowest Hartree-Fock total energy for formaldehyde so far. Comparison of our calculation A (basis 73/3/1) with the minimum Slater basis set results of Newton and Palke [21] shows clearly the superiority of the medium-sized Gaussian basis.

Detailed intermediate results: forces, energies and dipole moments at the equilibrium and displaced conformations are given only for the two larger basis sets in Table 3. Only two conformations have been calculated with the largest basis set C; this is sufficient to determine three force constants.

Table 4. Experimental force fields for formaldehyde^a

First author, set No., year, and Ref.	F_{11} CO	F_{12} CO/s.CH	F_{13} CO/s.bend	F_{22} s.CH	F_{23} s.CH/s.bend	F_{33} s.bend	F_{44} as.CH	F_{45} as.CH/rock	F_{55} Rock	F_{66} Wagging
Duncan (1973) [32] ^d	12.90	+0.811	+0.388	4.999	-0.122	0.572	4.872	+0.212	0.838	0.403
McKean, I (1971) [9] ^c	12.72	+0.610	+0.370	4.426	-0.091	0.543	4.391	+0.157	0.802	0.395
McKean, II (1971) [9]	13.56	+0.576	+0.776	4.421	-0.091	0.545				
Becher (1971) [10]	12.8	+0.45 ^b	+0.42	4.56	-0.24	0.510	4.53	+0.28	0.770	
Cossee,VF1(1966)[23]	12.72	0 ^b	+0.296	4.31	0 ^b	0.524	4.31	0 ^b	0.827	0.32
Cossee,VF2(1966)[23]	13.21	0 ^b	+0.43	4.31	0 ^b	0.513	4.31	0 ^b	0.835	0.32
Shimanouchi, I (1965) [24]	12.76	+0.96	+0.41	4.40	+0.18	0.560	4.33	-0.06	0.852	
Shimanouchi, II (1965) [24]	12.68	+0.97	+0.39	4.42	+0.16	0.560	4.31	-0.09	0.858	
Beckmann (1965) [25]	13.2	+0.33	+0.40	4.39	-0.32	0.504	4.37	-0.01	0.792	0.374
Mills (1963) [26]								+0.28		
Curtis, I (1964) [27]	12.8	+0.76	+0.39	4.41	+0.08	0.536	4.23	-0.15	0.83	
Curtis, II (1964) [27] ^d	13.0	+0.86	+0.49	5.16	0 ^b	0.632	5.03	0 ^b	0.94	
Oka (1961) [29]	12.37	-0.054	+0.333	4.41 ^b	+0.217	0.578	4.41 ^b	+0.377	0.793	0.341
Pillai (1961) [28]	12.1	+0.226	+0.267	4.40	0 ^b	0.447	4.252	0 ^b	0.681	0.308
Hisatsune (1955) [30]	12.3	0 ^b	+0.214	4.33 ^b	0 ^b	0.539	4.33 ^b	0 ^b	0.826	

^a In mdyn/Å, mdyn and mdynÅ for the stretching, stretching/bending and bending force constants, respectively.

^b Constrained values.

^c Only the A_1 species is given in [9], B_1 and B_2 were kindly passed on to us by Dr. J.L.Duncan.

^d With anharmonicity correction. See also Note added in Proof.

Experimental Force Fields

Before comparing our force constants to the experimental ones, we shall briefly discuss the latter. There are a number of force constant calculations for formaldehyde; the more recent ones are collected in Table 4. All force fields have been transformed to the following symmetry coordinates:

$$\begin{aligned}
 A_1 \text{ species: } & S_1(\text{CO}) = \Delta R \\
 & S_2(\text{s.CH}) = 2^{-1/2}(\Delta r_1 + \Delta r_2) \\
 & S_3(\text{s.bend}) = 6^{-1/2}(\Delta \beta_1 + \Delta \beta_2 - 2\Delta \alpha), \\
 B_1 \text{ species: } & S_4(\text{as.CH}) = 2^{-1/2}(\Delta r_1 - \Delta r_2) \\
 & S_5(\text{rock}) = 2^{-1/2}(\Delta \beta_1 - \Delta \beta_2), \\
 B_2 \text{ species: } & S_6(\text{wagging}) = \Delta \delta.
 \end{aligned}$$

Here R denotes the CO distance, r_1 and r_2 the CH_1 and CH_2 distances, respectively, β_1 the H_1CO angle, β_2 the H_2CO angle, α the HCH angle δ the angle of the CO bond with the CH_2 plane. Short descriptive names are given in parentheses.

Curiously there is little agreement between various experimental force fields: even the sign of several off-diagonal force constants varies. All calculations agree that F_{13} is positive and most of them put its value at about 0.4 mdyn. Calculations which do not neglect F_{12} completely agree that it is positive and fairly large (an exception is the Urey-Bradley force field of Oka and Morino [29]).

It should be mentioned that most force fields in Tab. 4 cannot be regarded as reliable by present standards. Most of them determine the force constants from vibrational frequencies of H_2CO and D_2CO . In principle this fixes the force field in the B_1 species. However, in the A_1 species these frequencies give only five independent pieces of information (the Teller-Redlich product rule must be obeyed) which is insufficient to determine the six A_1 species force constants. In practice it is almost impossible to determine even the B_1 species force field from the frequencies of the normal and deuterated molecule because of anharmonicity, as it has been pointed out by Chalmers and McKean [31]. Most authors do not mention at all how they circumvent this indeterminacy. We discard the results of Pillai and Cleveland [28] because they apparently contain an error². Most experimental force fields, including the recent one of Becher and Adrian [10], are based on old and poor geometry and on old frequency data. This impairs their accuracy.

In view of these shortcomings of the force fields available, we are very thankful to Duncan who has kindly agreed to perform an up-to-date force constant calculation and passed on to us his results for comparison with our theoretical values [32].

All experimental data now available were used in [32]: the frequencies of H_2CO and D_2CO , the ^{13}C shift of the 1746 cm^{-1} band in H_2CO , the observed ζ_{56} constant and the centrifugal distortion constants of H_2CO , H_2^{13}CO and D_2CO . Nevertheless, it was necessary to apply the Hybrid Orbital Force Field constraint [26], $F_{23} = -3^{-1/2} F_{45}$. Our *ab initio* results show that this constraint is roughly fulfilled. One may notice, however, that the constraint constant F_{45} shows the largest relative difference between the theoretical and experimental values.

Coupling Force Constants

The calculated and the most reliable experimental force constants are compared in Table 5. Agreement is good; it is especially significant that all coupling constants agree in sign with experiment. Agreement is very good for F_{13} which is determined most accurately by the experimental data. We conclude that our calculated coupling force constants are comparable in accuracy to the experimental values. Similar conclusions have been reached for other molecules [1–8].

We should like to emphasize that it is possible to decide merely on the basis of our calculations which of the two alternative force fields of McKean and Duncan [9] is the correct solution. These sets differ considerably in the value of F_{13} , the CO/s.bend coupling constant. Its calculated value (0.402–0.414 mdyne) agrees well with the set I value (0.37) but disagrees with the set II value (0.78). Apparently all experimental force fields are based on the right assignment and so the possibility of a set II-type solution might seem purely theoretical. In the analogous ethylene and diazomethane, however, the question of assignment had been open until recently [9, 7].

Table 5 shows that the results of calculation A (basis set 73/3/1) agree well with the force constants of the more sophisticated calculations B and C. This

² We have repeatedly checked our transformation to symmetry coordinates to see if the improbable results were caused by incorrect transformation. We were unable to find any mistake.

Table 5. Comparison of the experimental and calculated force constants of formaldehyde

Force constant	This work			Experimental ^b	Experimental ^c	Newton <i>et al.</i> [18]	Buenker <i>et al.</i> [22]	David [33]
	Set A	Set B	Set C					
F_{11} CO	13.905	13.646	13.663	12.90 ± 0.11	12.91 ± 0.08	17.8	14.34	28.7
F_{12} CO/s.CH	+0.676	+0.797	+0.791	$+0.811 \pm 0.112$	$+0.665 \pm 0.038$			
F_{13} CO/s. bend	+0.414	+0.411	+0.402	$+0.388 \pm 0.020$	$+0.414 \pm 0.073$			
F_{22} s.CH	4.999	4.885		4.999 ± 0.034	4.962 ± 0.024	6.9		5.7
F_{23} s.CH/s.bend	-0.106	-0.131		-0.122 ± 0.014	-0.123 ± 0.017			
F_{33} s.bend	0.645	0.634		0.572 ± 0.003	0.571 ± 0.003	0.743		2.1
F_{44} as.CH	4.909	4.791		4.872 ± 0.022	4.873 ± 0.025			
F_{45} as.CH/rock	+0.157	+0.146		$+0.212 \pm 0.025$	$+0.213 \pm 0.027$			
F_{55} rock	0.946	0.907		0.838 ± 0.003	0.835 ± 0.003			
F_{66} wagging	0.514	0.501		0.403 ± 0.002	0.403 ± 0.002		(0.40) ^d	

^a For units see Table 4.

^b Ref. [32], harmonic hybrid orbital force field (i.e. $F_{45} = -3^{1/2} F_{23}$), based on the data mentioned in text. See also Note added in Proof.

^c Ref. [32], harmonic hybrid orbital force field, based on solid state ^{13}C shifts of ν_2 in H_2CO and D_2CO instead of the gas phase frequency shift.

^d Calculated at $R_{\text{CO}} = 2.486$ Bohr.

shows, in agreement with results for other molecules, that force constants are not particularly sensitive to the basis set. Reasonable values can be obtained with basis sets like our set A. This allows the extension of the calculations to larger molecules. The inclusion of the d orbitals in addition to polarizing bond functions has a negligible effect on the three force constants calculated with d orbitals: on the CO stretching, the CO/s.CH coupling and the CO/s.bend coupling. In methane and ammonia inclusion of d functions produces several per cent change in diagonal bending force constants, without affecting the general nature of the force field [1, 2].

The sign of F_{23} (s.CH/s.bend) is negative and that of F_{45} (as.CH/rock) is positive both in our calculations and in the more reliable experimental force fields, and $|F_{23}| < |F_{45}|$. This is in accordance with the Hybrid Orbital Force Field model, suggested by Mills [26]. However, the exact magnitude of these constants, especially that of F_{23} is not well determined experimentally. Thus F_{23} is almost three times larger in Ref. [10] than in [9] or [32]. Our calculations make the lower value probable. Note that in several experimental force fields the signs of F_{23} and F_{45} are opposite to those above. We consider the evidence for the signs of these constants conclusive.

The most surprising feature in the force field of formaldehyde is the large positive coupling F_{12} between the CO and s.CH modes, both in the *ab initio* and in the experimental results. This is especially evident if one compares the force constants with those of ethylene. This is shown in Table 6 for the results obtained with 73/3/1 basis sets. It is clear that those calculations which constrain F_{12} to be zero are only crude approximations. Becher and Adrian [10] constrain F_{12} arbitrarily to be less than 0.5. Table 6 indicates that such a constraint cannot be justified.

Table 6. Comparison of the calculated force constants of ethylene and formaldehyde^a (basis set 73/3/1)

Force constant	Ethylene	Formaldehyde
C=X	9.94	13.91
s.CH	5.94	5.00
s.bend	0.556	0.645
C=X/s.CH	0.136	0.676
C=X/s.bend	0.242	0.414
s.CH/s.bend	-0.093	-0.106
as.CH	5.88	4.91
Rock	0.628	0.946
as.CH/rock	0.161	0.157
Wagging	0.322	0.514

^a Force constants in mdyn/Å, mdyn and mdynÅ for the stretching, stretching/bending and bending force constants, respectively. The definition of the coordinates for ethylene is analogous to those for formaldehyde (see Refs. [7, 8]).

In order to indicate a possible explanation for the large value of F_{12} we may note that our investigation of first row hydrides [6] showed a correlation between the stretch-stretch coupling constants and changes in the ionicity of the involved bonds. In fact, for formaldehyde we obtain the following derivatives of the Mulliken gross charges,

$$dq(\text{C})/dr_{\text{CO}} = 0.154 \text{ e/Bohr}$$

$$dq(\text{H})/dr_{\text{CO}} = -0.161 \text{ e/Bohr}$$

They are much larger than the corresponding values of ethylene:

$$dq(\text{C})/dr_{\text{CC}} = 0.042 \text{ e/Bohr}$$

$$dq(\text{H})/dr_{\text{CC}} = -0.021 \text{ e/Bohr}$$

This may also explain the 80% difference between the CO stretch/CH bend coupling constants. Apart from that, the force fields of ethylene and formaldehyde are quite similar.

Our calculations are consistent with the experimental data in that the CH/CH coupling, $1/2(F_{22} - F_{44})$ is small and positive. Calculations A and B give +0.045 and +0.047 mdyn/Å, respectively. The experimental value [32] is +0.063 ± 0.040 mdyn/Å.

Diagonal Force Constants

The calculated CO stretching force constant is 8% (calculation A) and 6% (calc. B and C) above the harmonically corrected experimental value [32]. The CH stretching constants are essentially correct. However, it is not very significant to compare diagonal stretching constants with experiment because anharmonicity makes the calculated value depend strongly on the internuclear distance used. The calculated CH stretching constants with basis set B are somewhat below the experimental value. This is probably due to the fact that our r_2 CH bond length exceeds slightly the true r_e bond length.

The diagonal bending constants are larger than the harmonically corrected experimental values [32] by 13% for the 73/3/1 basis (*A*) and by 11% (F_{33}) or 8% (F_{55}) for the 95/4/1 basis (*B*). Near-Hartree-Fock calculations on methane and ammonia [1, 2] show that an error of about +10% in these constants persists at the Hartree-Fock limit. Curtis [27] tried to correct for anharmonicity in his force field II. His values lie above the *ab initio* ones and this leaves little doubt that his anharmonicity corrections for the bending modes are too large.

Becher and Adrian [10] state that the CH stretching force constants are lower in formaldehyde than in ethylene, in spite of the shorter bond length in the former. This apparent contradiction is caused by the use of obsolete geometry data in [10]. According to more recent measurements [15] the CH bond is longer in H₂CO than in C₂H₄. This is in accordance with our *ab initio* geometry.

Like in ethylene, deviation from experiment is larger for the wagging force constant F_{66} (27 and 24%) than for the in-plane deformations. This might be caused by low-lying configurations of *B*₂ symmetry (involving the π^* orbital) which can mix to the Hartree-Fock determinant in non-planar conformations. Thus correlation may be more important for the out-of-plane deformations in π systems than for σ bonded molecules.

Comparison with Previous ab initio Force Constants

Some previous calculations of the force constants of H₂CO are collected in Table 5. Only diagonal force constants have been calculated so far, and the results deviate stronger from experiment than ours³. Even our 73/3/1 basis gives better CO stretching force constant than the 10,5/5 basis of Ref. [22] because it is not so heavily contracted and therefore more flexible.

Preliminary calculations with "minimal" Gaussian basis sets show that the poor results of David [3] cannot be ascribed to his basis set. Although agreement with experiment is worse with the minimal basis sets, the result, especially the bending force constants, are sensible. Thus it looks like the poor results of David are caused by the lack of SCF convergence which is mentioned in his paper.

Vibrational Frequencies

The vibrational frequencies of H₂CO and some of its isotopic derivatives have been calculated from the *ab initio* force field *A* (basis 73/3/1). In calculating vibrational frequencies we apply a simple empirical correction: diagonal stretching force constants are diminished by 10%, diagonal bending ones by 20% and the coupling constants are unchanged. This correction takes into account the influence of anharmonicity (which tends to lower the observed frequencies) and the fact that the calculated bending force constants are consistently too high. The results are shown in Table 7. For comparison, the frequencies of H₂CO are calculated also without this correction. The heavy isotope frequencies are given as frequency shifts relative to the unlabelled compound.

Agreement with experiment is good, as it is in the case of ethane, ethylene and acetylene [8]. For H₂CO the $\nu_5(B_1)$ frequency differs from the old experimental

³ The wagging force constant of Buenker and Peyerimhoff [22] agrees closely with the experimental figure. However, their value is not comparable to ours, neither to experiment, because it was obtained at a CO distance significantly larger than the experimental one.

Table 7. Calculated and observed frequencies and frequency shifts. Calculated frequencies are based on the corrected *ab initio* force field A (basis set 73/3/1), in cm^{-1}

Compound	$\nu_1(A_1)$	$\nu_2(A_1)$	$\nu_3(A_1)$	$\nu_4(B_1)$	$\nu_5(B_1)$	$\nu_6(B_2)$
H ₂ CO calc.	2799	1722	1474	2879	1207	1186
H ₂ CO obs. [35]	2766	1746	1501	2843	1247	1164
H ₂ CO obs. [34]	2780	1750	1503	2875	1278	1165
D ₂ CO calc.	2045	1678	1071	2145	955	951
D ₂ CO obs. [34]	2056	1700	1106	2160	990	938
HDCO calc. ^a	2842	1701	1363	2090	994	1075
HDCO obs. [36]	2844	1723	1400	2120	1041	1074
H ₂ ¹² CO–H ₂ ¹³ CO calc.	4.2	37.3	0.0	11.5	9.2	11.9
H ₂ ¹² CO–H ₂ ¹³ CO obs. [10]		37.9				
H ₂ C ¹⁶ O–H ₂ C ¹⁸ O calc.	0.0	37.2	6.9	0.0	5.0	1.3
D ₂ ¹² CO–D ₂ ¹³ CO calc.	13.9	27.5	1.2	16.8	9.3	15.0
H ₂ CO calc. with uncorrected force const.	2954	1849	1625	3037	1349	1326
H ₂ CO estimated harmonic frequencies [32]	2944	1773	1563	3009	1288	1191

^a In HDCO there is an *A'* species instead of *A*₁ and *B*₁.

value of Ebert and Nielsen by 71 cm^{-1} [34]. This is too large, taking into account that for ethane and ethylene the maximum deviation below 2000 cm^{-1} is 37 cm^{-1} [8]. The new assignment of Blau and Nielsen [35] gives an acceptable error of 40 cm^{-1} . It should be added that the experimental value of the ν_5 frequency is somewhat uncertain because the band is strongly perturbed.

Geometry

For basis set *B* we determined the fully optimized molecular geometry by the force relaxation method [13]. This method has converged in three iteration steps to 10^{-3} \AA in bond lengths and 0.1° in bond angle. The results of this converged calculation are given in Tab. 3 under the heading "calculated geometry". A final extrapolation using the forces in this calculation gives the following parameters: $R_{\text{CO}} = 1.1781 \text{ \AA}$, $r_{\text{CH}} = 1.0924 \text{ \AA}$, $\alpha_{\text{HCH}} = 115^\circ 54'$. The estimated experimental r_e values are as follows: $Y.203 \text{ \AA}$, 1.101 \AA and $116^\circ 31'$ [15]. The deviation is consistent with the observation that Hartree-Fock bond lengths are usually shorter than the experimental values whereas Hartree-Fock bond angles are very accurate. Our calculated angle corroborates the measurements of Takagi and Oka [15] and Oka [37] that the HCH angle is near 116° . A previous measurement [38] gave 118° . Interpolation from the forces obtained with basis set *C* predicts also $116^\circ 37'$ for the HCH angle (with bond lengths fixed at the experimental r_z values).

Dipole Moment Derivatives

Dipole moment derivatives and the connected infra-red intensities may be obtained from the dipole moments given in Tab. 3. They will be discussed in a separate paper together with results for other molecules.

Acknowledgement. We are very grateful to Dr. J. L. Duncan for calculating an up-to-date experimental force field for formaldehyde which made a real comparison of our results with experiment possible.

Note Added in Proof. After completion of this manuscript Duncan and Mallinson [39] have succeeded to obtain a complete and well-determined General Harmonic Force Field for formaldehyde by including new pieces of information (^{13}C shift of ν_1 in H_2CO , τ_{bbbb} of HDCO). The new off-diagonal constants are: $F_{12} = 0.739 \pm 0.06$, $F_{13} = 0.408 \pm 0.015$, $F_{23} = -0.077 \pm 0.045$, and $F_{4,5} = 0.171 \pm 0.037$. Agreement with the theoretical values of $F_{4,5}$ is now substantially better.

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