

***Ab initio* Study, Including Electron Correlation, of the Electronic Structures, the Dipole Moments, the Static Polarizabilities and of the Harmonic Force Fields of H₂CO, H₂CS and H₂SiO**

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Ab initio calculations including electron correlation (on the PNO-CI and CEPA-PNO levels) are carried out for the isovalence electronic molecules H₂CO, H₂CS and H₂SiO, and for comparison also for H₂O and CO. The CEPA equilibrium distances are accurate to within 0.003 Å, while SCF results show significantly larger errors. The harmonic force constants on CEPA level are satisfactory as well, but for stretching of double or triple bonds inclusion of singly substituted configurations is imperative. Dipole moments were obtained with an error of ≈ 0.1 Debye from CEPA calculations with sufficiently large basis sets and inclusion of singly substituted configurations. The dipole polarizabilities are less sensitive to correlation effects but require larger basis sets.

The population analysis reveals that the SiO bond in H₂SiO is highly polar and that *d*-AO's cannot be regarded as valence AO's in any of the molecules of this study. The binding energy of H₂SiO (with respect to H₂Si(¹A₁) + O(³P)) is predicted as 140 ± 5 kcal/mol. The contributions of different pairs in terms of localized orbitals to the correlation energy of the molecules of this study are analyzed.

Key words: Formaldehyde – Thioformaldehyde – Prosiloxane – Silanone

1. Introduction

Formaldehyde H₂CO and thioformaldehyde H₂CS have often been studied by quantum chemical methods, mainly because they are the prototypes of compounds with CO and CS double bonds which are very important in organic chemistry [1, 2]. Thioformaldehyde has long been unknown (at least not known in pure form) experimentally. Its recent synthesis in pure monomeric form was successful only after H₂CS and possible contaminations could be identified via the PE spectrum predicted from an *ab initio* calculation [3]. Silanone (prosiloxane) H₂SiO is supposed

to be an intermediate in chemical reactions leading to polymeric $(\text{H}_2\text{SiO})_n$, as e.g. $\text{SiH}_2\text{Br}_2 + \text{H}_2\text{O} \rightarrow 2\text{HBr} + \text{H}_2\text{SiO} \rightarrow 2\text{HBr} + (1/n) (\text{H}_2\text{SiO})_n$ [4].

Our study of formaldehyde and its analogues had several motives:

1. We have been interested in differences between bonding of first-row and second-row elements, especially in the different role of *d*-AO contributions. The comparison of H_2CO with either H_2CS or H_2SiO is hence complementary to the comparison of H_3PF_2 with H_3NF_2 [5] and of H_3PO with H_3NO [6]. While in these hypervalent molecules the different role of *d*-AO's is pronounced, no significant difference in the *d*-contributions is found for the normalvalent molecules H_2CO and H_2CS , whereas H_2SiO is not directly comparable to H_2CO , since the SiO bond is highly polar.

2. We have recently analyzed the correlation energy of a few hydrides [7, 8] and of small molecules with one single or multiple homonuclear bond, like ethane, ethylene and acetylene [9]. An extension of this analysis to heteronuclear double bonds seemed in order.

3. The physical properties of formaldehyde are known to a high degree of accuracy from experiment. This molecule serves hence as a good test case for sophisticated quantum mechanical methods. Neither the equilibrium geometry nor the dipole moment are well accounted for by near Hartree–Fock calculations [2] and methods that strive for high accuracy have not been applied to formaldehyde so far. We therefore want to test the CEPA method [10, 11] on formaldehyde before applying it to predict certain properties of thioformaldehyde and prosiloxane.

4. The *ab initio* calculation of force constants and vibrational frequencies still poses serious problems. There is no doubt that the Hartree–Fock approximation is unsatisfactory, but even the inclusion of electron correlation on CEPA level [10, 11] has not been fully reliable for multiple bonds, as we have e.g. observed for N_2 [9], whereas for single bonds CEPA appears to be nearly perfect [12, 13]. We have therefore included in our study H_2O as a molecule with only single bonds and CO as a molecule with a multiple bond similar to that in H_2CO .

5. In a recent study Ahlrichs and Heinzmann [14] have analyzed the Si=C double bond. It is interesting to compare this with the isoelectronic Si=O bond.

2. Method and Basis Sets

We have used the SCF, IEPA-PNO, CEPA-PNO and PNO-CI methods that are described elsewhere [11] in detail. The three latter methods take care of electron correlation effects on the basis of PNO's (pair natural orbitals). Experience has shown that CEPA is the most reliable of the three PNO approaches, one reason for this being that it has the correct dependence on the number of particles. To be more precise we use the variant CEPA-2 (for a comparison of different CEPA variants see Ref. [15]).

In standard CEPA (or PNO-CI) calculations we only include doubly substituted configurations (and in CEPA implicitly unlinked clusters of double substitutions), but we have also performed calculations with the inclusion of single substitutions.

All PNO-configurations were included that contribute to the energy more than 10^{-6} Hartree, but never more than 30 PNO's per pair.

The basis set consists of Gaussian lobes, from which *p*, *d* or *f* type AO's are constructed as indicated previously [16]. Standard basis sets of Huzinaga [17] were augmented by the polarization functions optimized previously [7–9]. The basis sets for the three molecules are given in Table 1. The size of the basis sets for one molecule increases in the order A, B, C. One notes that for H₂SiO, in view of the large negative charge on O, flat *s* and *p* functions have to be included.

Table 1. Basis sets

H₂CO, H₂O and CO, basis A

C: (4, 3 × 1; 2, 1; 1) $\eta_a = 0.7$

O: (4, 3 × 1; 2, 1; 1) $\eta_a = 1.25$

H: (2, 1; 1) $\eta_p = 0.75$

H₂CO, H₂O and CO, basis B: polarization functions as basis A

C, O: (5, 4 × 1; 3, 2 × 1; 1)

H: (3, 2 × 1; 1)

H₂CO, CO, basis C: as basis B, but two sets of polarization functions per atom

C: $\eta_a = 0.2; 0.7$

O: $\eta_a = 0.3; 1.25$

H: $\eta_p = 0.21; 0.75$

CO, basis C': as basis C, but with contraction

C, O: (4, 5 × 1; 2, 3 × 1)

CO, basis D: as basis B, but three sets of polarization functions per atom

C: $\eta_a = 0.06; 0.18; 0.7$

O: $\eta_a = 0.104; 0.313; 1.25$

H₂O, basis D

O: (5, 4 × 1; 3, 2 × 1; 3) $\eta_a = 0.104, 0.313; 1.25$

H: (3, 2 × 1; 2) $\eta_p = 0.21; 0.75$

H₂O, basis E: as basis D, but with additional "flat functions" on oxygen

O: $\eta_s = 0.1; \eta_p = 0.07$

H₂CS, H₂SiO, basis A: C, O, H as H₂CO, basis A

S: (4, 6 × 1; 3, 3 × 1; 1) $\eta_a = 0.55$

Si: (4, 6 × 1; 3, 3 × 1; 1) $\eta_a = 0.5$

H₂CS, basis B: as basis A, but two sets of polarization functions per atom

S: $\eta_a = 0.157; 0.55$

C: $\eta_a = 0.2; 0.7$

H: $\eta_p = 0.21; 0.75$

H₂SiO, basis B: as basis A, but with additional "flat" *s* and *p* functions on

O: $\eta_s = 0.1; \eta_p = 0.1$

H₂SiO, basis C: additional flat functions as basis B

Si: (5, 6 × 1; 4, 3 × 1; 1) $\eta_a = 0.5$

O: (5, 4 × 1; 3, 2 × 1; 1) $\eta_a = 1.25$

H: (3, 2 × 1, 1) $\eta_p = 0.75$

3. Equilibrium Geometries

The equilibrium geometries were found by a multi-dimensional polynomial fit to the energies of a sufficient number of structures of A_1 symmetry. These geometry optimizations were done on the SCF, IEPA, CI and CEPA levels. The results are compared in Table 2 to values from experiment. As far as experimental values are concerned the difference between r_e - and r_0 (or rather r_2)-geometries [18] has to be kept in mind, since quantum chemical calculations always yield the r_e -geometries.

In comparing our geometrical parameters with those of previous calculations (Ref. [2], Table II) one has to keep in mind that often some parameters were imposed and not varied.

One realizes that the agreement between the CEPA values with basis B for the interatomic distances and the experimental r_e is nearly perfect, the differences are of

Table 2. Equilibrium geometries^a

H ₂ CO	SCF		PNO-CI	CEPA-PNO		experimental			
	basis A	basis B	basis B	basis A	basis B ¹	r_2^b	r_2^c	r_2^e	
	r_{CO}	1.177	1.179	1.194	1.199	1.207	1.2078	1.207	1.202
	r_{OH}	1.103	1.094	1.100	1.104	1.1160	1.1160	1.117	1.100
$\angle HCH$	114.3	115.9	115.8	114.0	116.0	116.5	116.2	116.3	
H ₂ CS	SCF		PNO-CI	CEPA-PNO	experimental				
	basis A		basis A	basis A	r_2^d				
	r_{CS}	1.594	1.602	1.613	1.611				
	r_{CH}	1.084	1.092	1.095	1.093				
$\angle HCH$	115.2	115.1	115.3	116.9					
H ₂ SiO	SCF		PNO-CI	CEPA-PNO					
	basis A		basis A	basis A					
	r_{SiO}	1.485	1.499	1.507					
	r_{SiH}	1.472	1.473	1.471					
$\angle HSiH$	109.9	109.7	110.0						
H ₂ O	SCF			CEPA-PNO		experimental			
	basis A	basis B		basis A	basis B	r_0^f	r_2^g		
	r_{OH}	0.947	0.942		0.962	0.957	(0.956)	0.958	
	$\angle HOH$	102.6	106.3		100.2	104.1	(105.2)	104.5	
CO	SCF			CEPA-PNO		experimental			
	basis A	basis C'		basis A	basis C' ¹	r_0^h	r_2^h		
	r_{CO}	1.107	1.107		1.127	1.137	1.131	1.128	

^a Distances in Å, angles in degrees.

^b Ref. [30].

^d Ref. [32].

^f Ref. [40].

^h Ref. [33].

^c Ref. [31].

^e Ref. [33].

^g Ref. [52].

¹ With single excitations.

the order of 0.002 Å, i.e. one order of magnitude smaller than the corresponding errors of the SCF values. This confirms similar results by Meyer *et al.* on diatomic molecules [12].

One notes that (this is not documented in Table 2, see however Ref. [2], Table II) the inclusion of polarization functions in the basis is very important, but also that as far as the *s-p*-part of the basis is concerned, the (7, 3) basis – which has turned out to be quite satisfactory for hydrocarbons [9, 19] – is not good enough for oxygen compounds, where the (9, 5) basis has to be used.

The apparently excellent agreement between the CEPA geometry for H₂CS with the experimental *r_e*-geometry is probably fortuitous since something similar is observed for H₂CO with basis A. A larger H₂CS basis comparable to basis B has probably to be used to obtain an accurate *r_e*-geometry.

For H₂SiO no experimental values are available for comparison, but one may quote *r₀*(SiH) = 1.48 Å [20] or 1.45₆ Å [4, 33] in SiH₄ and *r_e*(SiH) = 1.508 Å in SiH₂ [21] while *r_e*(SiO) in SiO is 1.510 Å [4]. That *r*(SiH) is smaller in H₂SiO than in SiH₂ is understandable in view of the “*sp*² hybridization” vs. “pure *p*-bonds”.

The shorter CH bond length in H₂CS as compared to H₂CO is an indication of a stronger CH bond in H₂CS.

In all the H₂XY molecules correlation lengthens the XY-bond while it has little effect on the XH bond lengths and the angles.

4. Harmonic Force Constants and Vibrational Frequencies

The harmonic force constants are defined as the (mixed) second derivatives of the energy *E*(*q*₁, ..., *q*_{*n*}) with respect to internal coordinates *q_k*:

$$f_{kl} = \left(\frac{\partial^2 E}{\partial q_k \partial q_l} \right)_0.$$

Symmetry force constants *F_{kl}* are analogously defined with respect to internal symmetry coordinates *Q_k*. For H₂XY molecules the symmetry coordinates are

- A*₁: *Q*₁: XY-stretching
- Q*₂: symmetric XH-stretching
- Q*₃: symmetric HXH-bending
- B*₂: *Q*₄: antisymmetric XH-stretching
- Q*₅: YXH-bending
- B*₁: *Q*₆: out-of-plane bending.

We proceed by computing *E* for a sufficient number of nuclear configurations and constructing a multidimensional polynomial fit for *E* (*Q*₁, ..., *Q*_{*n*}). The same fit that is needed for finding the equilibrium geometry, also furnishes the *F_{kl}* of *A*₁ symmetry. The following variations of lengths and angles turned out to be optimum: Δ*9* ≈ 0.04 *a*₀, Δ*α* ≈ 2°.

Alternatively to this “energy method” one can use the “force method” [22, 23] in which one starts by computing not just E but also the $\partial E/\partial Q_k$ for the selected nuclear configurations. The analytical fits to the $\partial E/\partial Q_k$ need then only be differentiated once to yield the F_{ki} . This alternative is rather appealing but has the disadvantage that at present it is only applicable in the context of the SCF method. Correlation effects can so far only be dealt with by the energy method.

The force constants from the present study are compared in Tables 3 to 7 with values from the literature.

Table 3. Harmonic force constants (in terms of symmetry coordinates) for H_2CO^a

basis	SCF	SCF at CEPA-Min.		CEPA		Meyer, ^b	experiment ^c
	A	A	B	A	B ^d	Pulay	
A ₁ F_{11}	16.72	14.89	14.69	14.75	13.35	13.91	12.90
F_{12}	1.08	0.86	0.80	0.88	0.83	0.68	0.74
F_{22}	5.40	5.00	5.06	4.85	4.92	5.00	4.96
F_{13}	0.28	0.41	0.41	0.40	0.41	0.41	0.41
F_{23}	-0.07	-0.12	-0.13	-0.11	-0.13	-0.11	-0.08
F_{33}	0.69	0.65	0.59	0.63	0.59	0.65	0.57
B ₂ F_{44}	5.18	4.87	5.03	4.83	4.90	4.91	4.85
F_{45}	0.16	0.15	0.14	0.14	0.14	0.16	0.17
F_{55}	0.95	0.92	0.91	0.89	0.88	0.95	0.83
B ₁ F_{66}	0.52	0.50	0.49	0.46	0.43	0.51	0.40

^a In mdyne/Å, mdyne/rad, mdyne Å/rad².

^b Ref. [34] Force method. SCF at experimental geometry.

^c Ref. [31].

^d Inclusion of single excitations for the CO stretching vibration; fit with 4th degree. The average of the two fits of 3rd and 4th degree is 13.4.

Table 4. Harmonic force constants (in terms of symmetry coordinates) for H_2CS^a

basis	SCF	SCF at CEPA-geom.		CEPA	Bruna	<i>et al.</i> ^b	experiment ^c
	A	A		A	SCF	CI	
A ₁ F_{11}	8.49	7.50		7.17	7.0	6.46	6.0–6.8
F_{12}	0.22	0.20		0.22			
F_{22}	5.94	5.74		5.78			
F_{13}	0.27	0.26		0.29			
F_{23}	-0.15	-0.15		-0.14			
F_{33}	0.54	0.54		0.53			
B ₂ F_{44}		5.58		5.59			
F_{45}		0.06		0.10			
F_{55}		0.63		0.62			
B ₁ F_{66}		0.38		0.32			

^a Dimensions as in Table 3.

^b Ref. [35].

^c Ref. [37].

Table 5. Harmonic force constants (in symmetry coordinates) for H₂SiO.^a

basis	SCF		SCF at CEPA geom.		CEPA		Kramer ^b
	A	A	A	A	A	A	
A ₁ F ₁₁	12.12		10.57		10.52		8.90
F ₁₂	0.58		0.12		0.10		0.07
F ₂₂	3.14		3.19		3.08		3.04
F ₁₃	0.15		0.15		0.15		0.08
F ₂₃	-0.25		-0.06		-0.05		-0.06
F ₃₃	0.54		0.55		0.53		0.59
B ₂ F ₄₄			3.15		3.03		3.29
F ₄₅			0.07		0.12		0.06
F ₅₅			0.62		0.61		0.59
B ₁ F ₆₆			0.41		0.36		0.21 ^c

^a Dimensions as Table 3.

^b Ref. [36]. Force method. SCF at $\alpha = 112^\circ$, $r_{\text{SiO}} = 1.59 \text{ \AA}$, $r_{\text{SiH}} = 1.48 \text{ \AA}$.

^c Inconsistent with the B₁ frequency given by the same author.

Table 6. Harmonic force constants (in terms of internal coordinates) for H₂O^a

basis	SCF		SCF at CEPA geom.		CEPA		Pulay ^b		experiment	
	A	B	A	B	A	B	A	B	^c	^d
F ₁₁	9.35	9.79	8.49	8.87	8.44	8.80	9.33	9.16	8.46	8.45
F ₁₂	-0.09	-0.08	+0.04	-0.06	-0.09	-0.13	-0.16	-0.17	-0.10	-0.10
F ₁₃ /R _e	0.26	0.25	0.19	0.25	0.26	0.27	0.29	0.30	0.25	0.23
F ₃₃ /R _e ²	0.93	0.85	0.95	0.84	0.89	0.83	0.83	0.85	0.76	0.76

^a Dimensions as Table 3.

^b Ref. [38].

^c Ref. [39].

^d Ref. [40].

Table 7. Harmonic force constant for CO (in mdyn/Å)

Basis	SCF		CI		CEPA		FOCI Kirby-Docken		experiment ^c
	A	C'	A	C' ^d	A	C' ^d	Liu ^b		
	24.26	23.57	19.26	22.27	20.71	21.38	18.97	18.60	19.00

^a At the CEPA minimum.

^b Ref. [41]. We have calculated F from the points in [41], first-order CI, using the same fit as for our CEPA potential curve.

^c Ref. [33].

^d Inclusion of single excitations.

For H_2CO one finds good agreement between the CEPA results and the experimental values. For the stretching force constants of the CO bond singly substituted configurations have to be included; they reduce the error in F_{11} from 12% to about 4%. The same holds (even to a larger extent) for the CO force constant in carbon monoxide.

The SCF results are, on the whole, much poorer than the CEPA values (too large for all diagonal elements, for f_{CO} the error is e.g. $\sim 26\%$). It is interesting to note that, if one calculates the F_{pq} from a fit to SCF points as the second derivatives not at the optimum SCF geometry, but at the CEPA or the experimental geometry, the agreement with experiment is much better, and almost as good as from full CEPA calculations. The reason for this is that correlation only affects the energy and its first derivatives with respect to the Q_k but hardly the second derivatives (see Fig. 1) such that it shifts the equilibrium geometry but not $\partial^2 E / \partial Q_k \partial Q_l$ at a given geometry.

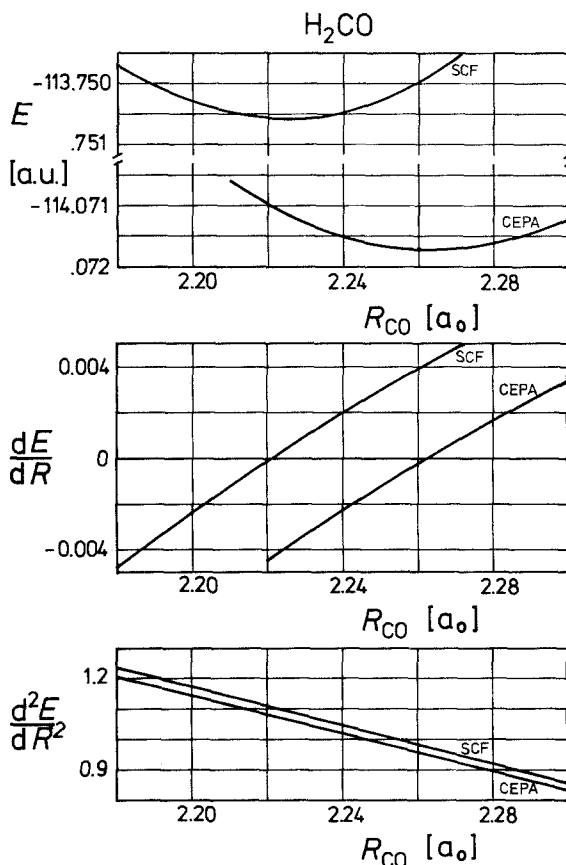


Fig. 1. The dependence of the total energy and its first and second derivatives with respect to R on the C—O distance R in H_2CO ; SCF and CEPA approximations; basis B; atomic units

This fact has previously been exploited by Pulay [22] who evaluated F_{pq} rather successfully from SCF calculations at the experimental equilibrium geometries.

The harmonic vibration frequencies of the molecules in this study are given in Table 8. CEPA with basis B gives values that differ from the experimental counterparts only by a few percent.

The force constants and harmonic vibration frequencies for H₂O on the same level of approximations (Table 6) are of similar quality, again with a noticeable improvement through the inclusion of correlation effects.

For H₂CS little is known from experiment about the force field. Our values in Table 4 have therefore to be regarded as predictions. The same is true for H₂SiO for which the results are given in Table 5.

The IR spectrum of impure H₂CS has been studied by several authors [37, 56], but the assignment is rather dubious. Our results in Table 8 indicate that the weak band

Table 8. Harmonic vibration frequencies in cm⁻¹

H ₂ CO basis	SCF	SCF at CEPA-geom.	Meyer, ^a	CEPA	experiment ^b	
	A	B	Pulay	B	harmonized	measured
A ₁	2059.2	1882.6	1849	1797.2	1763.7	1746.0
	3066.1	2971.2	2954	2925.6	2944.3	2782.4
	1687.1	1600.1	1625	1580.9	1562.6	1500.0
B ₂	3115.0	3070.6	3037	3032.3	3008.7	2843.2
	1376.4	1349.7	1349	1308.9	1287.7	1247.1
B ₁	1316.2	1301.4	1326	1220.9	1191.0	1167.2

H ₂ CS basis	SCF	SCF at CEPA-geom.	CEPA	experiment ^c	
	A	A	A	^d	^e
A ₁	1202	1134.3	1112.9	(1150)	1063
	3231	3200.0	3214.5	2971	2970
	1597	1577.3	1566.7	(1550)	
B ₂		3216.9	3211.9	3025	3028
		1051.2	1039.6	1438	1437
B ₁		1013.8	1119.9	(1100)	993

H ₂ SiO basis	SCF at CEPA-geom.	Kramer ^f	CEPA
	A	A	A
A ₁	1325.0	1171.4	1320.0
	2354.0	2288.2	2314.2
	1141.1	1036.9	1127.9
B ₂	2348.5	2297.3	2296.8
	785.6	692.6	778.3
B ₁	771.0	1000.4 ^g	721.9

(continued)

Table 8 (*continued*)

H ₂ O basis	SCF		CEPA		CI-SDQ ^l		experiment ^h
	A	B	A	B			
A ₁	1836.6	1752.2	1791.2	1732.1	1687.1	1670.1	1648.5
	4040.4	4130.8	3842.8	3910.4	3855.1	3868.9	3832.2
B ₂	4136.9	4236.9	3928.6	4026.5	3958.5	3980.2	3942.5

CO basis	SCF	CEPA		PNO-CI		other CI ⁿ	experiment ^k
	C'	A ^j	C' ^m	C'			
ω_e	2415.4	2294.5	2167.3	2264.0			2170.21
$\omega_e x_e$	13.24	14.6	14.96	13.68			13.46
ν^l	2388.9	2264.2	2137.4	2236.6	$\left\{ \begin{array}{l} 2128.3 \text{ (VCI)} \\ 2140.6 \text{ (FOCI)} \\ 2235.9 \text{ (SDCI)} \end{array} \right.$		2143.3

^a Ref. [34]. Force method. SCF at experimental geometry. ^bRef. [31].

^c Not harmonized. Assignment as given by the authors.

^d Ref. [56]. ^e Ref. [37]. ^f Ref. [36]. Force method.

^g See footnote c on Table 5. ^h Ref. [39].

ⁱ CI calculations using singly, doubly and quadruply excited configurations and very large basis sets. First column Ref. [42], second column Ref. [57].

^j Without single substitutions. ^kRef. [33]. ^l $\nu = \omega_e - 2\omega_e x_e$.

^mFit with 4th degree, the averaged value between 4th and 5th degree is $\omega_e = 2166.3$, $\omega_e x_e = 13.72$.

ⁿ Ref. [41], VCI = valence CI, FOCI = first order CI, SDCI = singles doubles CI.

observed at 2874 cm^{-1} [37] cannot be due to the overtone $2\nu_6$, but possibly $2\nu_3$. Furthermore, there should be three bands between about 950 and 1100 cm^{-1} ; only two of them have been observed [37].

Comparison of the force fields of H₂CO, H₂CS and H₂SiO indicates a decrease of the XY stretching force constants in the order CO, SiO, CS and a decrease of the XH stretching force constants in the order H₂CS, H₂CO, H₂SiO. The larger force constants for H₂CS as compared to H₂CO is consistent with the smaller CH bond length in H₂CS. The bending force constants vary little in the three molecules and also the coupling constants show a very similar pattern, with the exception of F_{12} , which is much larger in H₂CO than in H₂CS or H₂SiO and which demonstrates a relatively large coupling between the CH and CO bonds.

On the whole, electron correlation reduces all diagonal force constants somewhat, but the XY stretching constant to a larger extent.

5. Dipole Moments

The dipole moment is an expectation value of a one-particle operator and one should hence expect that the SCF approximation should furnish good results. To under-

stand why this is often not the case one has to remember that the dipole moment is a difference of two large contributions with opposite sign, an electronic contribution that depends on the quality of the wave function and a nuclear contribution that is independent of it.

One sees from Table 9 that electron correlation reduces the dipole moments of H₂CO and CO by roughly 0.5 Debye. For CO it leads even to sign inversion. The dipole moment of H₂O, on the other hand, is only slightly affected by correlation.

Although the correlation effect on the energy comes mainly from doubly substituted configurations and only to a very small extent from single substitutions, the relative importance of the two types of substituted configurations is inverted for dipole moments [24]. It is hence imperative to include singles.

Before one considers correlation effects one has to check whether the basis is sufficiently close to saturation for the SCF part. Basis sets which are just good enough for the energy are usually too poor for dipole moments. As a rule of thumb [25] one may say that when for the energy one set of polarization functions per atom is necessary, one needs two such sets for the dipole moment and even three sets for polarizabilities (see the following section). For large or even medium-sized molecules one can normally not afford sufficiently saturated basis sets. One may hope, however, that for larger molecules the interatomic charge displacement becomes more important for the dipole moment (and the polarizability) than the intraatomic deformation of the orbitals, such that larger molecules do not require too excessive basis sets. The rather good results for H₂CO and H₂CS with not very large basis sets seems to confirm this.

In comparing computed with experimental dipole moments one has to keep in mind that the latter are averaged over the zero-point vibrations and are close to the theoretical values for the r_z rather than the r_e -geometry.

Corrections for zero-point vibrations have been discussed [25], but in the present case they can be estimated to change the dipole moments at most by 2 to 4%.

One technical remark has to be made, concerning the evaluation of expectation values within the CEPA scheme. It is straightforward to compute the one-particle density matrix and expectation values of one-particle operators in the PNO-CI scheme, since the PNO-CI wave function is well defined. CEPA is, however, a method to compute approximate total energies and it is not obvious to which wave functions this corresponds.

Our philosophy is (see e.g. Ref. [15]) that in CEPA one computes approximately a wave function of the form

$$\Psi^{\sigma} = e^{\sigma} \Phi$$

$$\sigma = \sum_{i < j} \sum_{a < b} f_{ij}^{ab} [a_a^+ a_b^+ a_j a_i - a_i^+ a_j^+ a_b a_a] + \sum_{i,a} f_i^a [a_a^+ a_i - a_i^+ a_a]$$

where i, j refer to spin orbitals occupied in Φ , a, b to those unoccupied in Φ . The coefficients f_{ij}^{ab} are generated in the CEPA formalism, they have hence to be

Table 9. Dipole moments (in Debye)

method	SCF near the SCF-minimum			SCF at CEPA-minimum			PNO-CI			CEPA			other theoret.	experiment		
	A	B	C	A	B	C	A	B	C	A	B	C				
H ₂ CO	2.330			2.422	2.821	2.747				2.236 ^m	2.387 ^m	2.412 ^m	2.219 ^m	2.759 ^e , 2.86 ^d	2.39 ^a	
H ₂ CS	1.983			2.034	1.999		1.799 ^a		1.794 ^o			1.583 ^b	1.493 ^o	1.205 ^e , 1.58 ^f	1.647 ^b	
H ₂ SiO	3.404	4.388	4.430	3.489	4.493	4.526								4.203 ^e		
basis	B	D	E	B	D	E	B	D	E	B	D	B	D	E		
H ₂ O	2.151			2.201	1.965	1.994	2.102	1.864	1.897	2.076	1.836	1.870	1.870	1.987 ^h	1.836 ⁱ	1.82 ^a
basis	B	C	D	B	C	D	B	C	D	B	C	D	D			
CO	-0.207	-0.141	-0.144	-0.313	-0.241	-0.245	0.085	0.126	0.117	0.254	0.289	0.275	0.275	0.082 ^j	0.310 ^k	0.112 ± 0.005 ^a

^a Ref. [43].^o Ref. [34], SCF.^e Ref. [50], "FGSO".^f Ref. [36], SCF, very small basis.^g Ref. [25], CEPA-1.^h Ref. [25], CEPA-1.^m H₂CO: $r_{CO} = 1.202$ Å for PNO-CI and CEPA.ⁿ r_{CS} , α experimental values; $r_{CH} \approx 1.092$ Å.^o Exp. geometry.^b Ref. [32].^d Ref. [49], "SCF limit".^f Ref. [51], minimal basis SCF.^g Ref. [25], SCF.ⁱ Ref. [41], "SDCI".^j CO: $r_{CO} = 1.128$ Å for PNO-CI and CEPA, $r_{CO} \approx 1.107$ Å for SCF.

inserted into the above formula. Expectation values are then given by the Hausdorff-formula

$$\langle Y|A|Y\rangle = \langle \Phi|A|\Phi\rangle + \langle \Phi|[A, \sigma]|\Phi\rangle + \frac{1}{2}\langle \Phi|[[A, \sigma], \sigma]|\Phi\rangle + \dots$$

Since one truncates the expansion of the energy at the second-order in σ , other expectation values should as well be evaluated up to second-order in σ .

If we write

$$\Phi_1 = \left\{ \sum_{i < j} \sum_{a < b} f_{ij}^{ab} a_a^+ a_b^+ a_j a_i + \sum_{i, a} f_i^a a_a^+ a_i \right\} \Phi$$

the expectation value of the dipole moment operator A is for a CEPA-PNO wave function evaluated as

$$\langle A \rangle = \langle \Phi|A|\Phi\rangle \cdot \{1 - \langle \Phi_1|\Phi_1\rangle\} + 2\langle \Phi|A|\Phi_1\rangle + \langle \Phi_1|A|\Phi_1\rangle$$

while for PNO-CI wave functions the standard expression

$$\langle A \rangle = \{ \langle \Phi|A|\Phi\rangle + 2\langle \Phi|A|\Phi_1\rangle + \langle \Phi_1|A|\Phi_1\rangle \} / \{1 + \langle \Phi_1|\Phi_1\rangle\}$$

is used. The bulk of the correlation correction comes in either case from the singly substituted configurations $\Phi_1^{s\sigma}$ in Φ_1 i.e.

$$\langle \Phi|A|\Phi_1^{s\sigma}\rangle = 2 \sum_{i, a} f_i^a \langle i|A|a\rangle.$$

Our best results for the dipole moments (CEPA, basis C) differ from the experimental values by ~ 0.1 Debye. One also sees from Table 9 that the CEPA results with basis B are still quite acceptable, the SCF values are poorer. Surprisingly, in H₂CO and CO the CI values are much closer to experiment than the CEPA values [25].

Figure 2 contains our results for the dipole moment curve of CO, calculated with basis D, between 1.9 and 2.5 a_0 . For comparison we have also included the curves

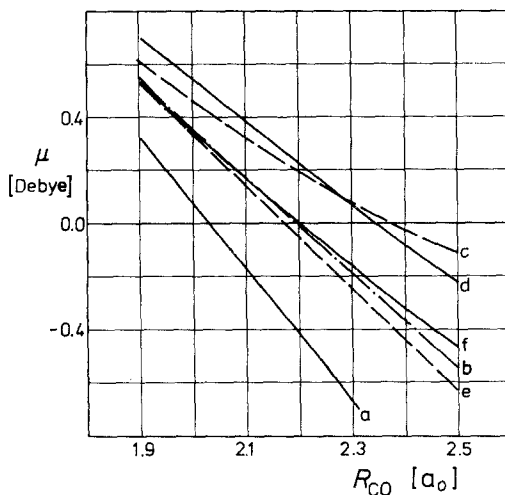


Fig. 2. Dipole moment curves for CO: *a*) SCF, basis D, *b*) PNO-CI, basis D, *c*) CEPA basis D, *d*) First-order CI, Ref. [41], *e*) CI with singles and doubles, Ref. [41], *f*) Exp., Ref. [58]

obtained by Kirby–Docken and Liu [41] with first-order CI (FOCI) and CI including all singles and doubles (SDCI) and the experimental curve of Chackerian [58]. As it can be expected the CEPA and FOCI curves agree fairly well, so do even better the PNOCI and SDCI curves. It is slightly surprising that the experimental curve coincides with PNOCI and not with the CEPA curve, though in all other cases so far the CEPA approximation has proved superior to PNOCI. The failure of CEPA for the dipole moment of CO has also been noted by other authors [25, 59].

6. Dipole Polarizabilities

The dipole polarizability tensor α has its principle axes determined by symmetry for all molecules of this study. We choose the twofold symmetry axis as z , the axis perpendicular to z in the molecular plane as y and the axis perpendicular to the molecular plane as x .

The computation of α can be done in two equivalent ways, either by perturbation theory with a static field as perturbation, or by the method of “finite perturbations”, i.e. from variational calculations of the molecule with and without an external field (properly for different field strengths and extrapolation to zero field strength).

A rigorous perturbation approach including electron correlation effects is at present not available, such that we had to choose the method of finite perturbations. This can be applied in two ways:

- a) One computes the energy $E(\vec{\mathcal{E}})$ for different values of the electric field strength $\vec{\mathcal{E}}$, constructs an analytic fit for $E(\mathcal{E}_x, \mathcal{E}_y, \mathcal{E}_z)$ and from it the second derivatives $\alpha_{xx} = \partial^2 E / \partial \mathcal{E}_x^2$ etc.
- b) One computes the effective dipole moment $\mu_{\text{eff}} = \mu_{\text{perm}} + \mu_{\text{ind}}$ and then the polarizability as first derivative of μ_{eff} with respect to $\vec{\mathcal{E}}$,

$$\text{e.g. } \alpha_{xy} = \frac{\partial \mu_{\text{eff},x}}{\partial \mathcal{E}_y}$$

It turned out that the method (b) has the advantage of being numerically much more stable than method (a) and further that μ_{ind} is practically linear for field strengths of $\lesssim 10^{-2}$ a.u. (1 a.u. = $e/a_0^2 \simeq e/(4\pi\epsilon_0 a_0^2) \simeq 5.144 \cdot 10^{11} \text{ Vm}^{-1}$). It is hence sufficient to compute just one point per direction (x, y, z) for a field strength between 10^{-4} to 10^{-2} a.u.

It has already been mentioned in the last section that three sets of polarization functions per atom are necessary [25] in order to obtain good dipole polarizabilities.

Correlation effects are, on the whole, not very large (10–20%), but the bulk of the correlation contributions ($\sim 90\%$) comes from singly substituted configurations.

With unsaturated basis sets one obtains in general too small polarizabilities, although it seems that (as for dipole moments) for large molecules relatively smaller basis sets may be sufficient. The basis unsaturation is usually different for the components of the polarizability in different directions, such that the average polarizability is usually obtained more reliably than the anisotropy.

Table 10. Static dipole polarizabilities in atomic units (at the experimental geometries)

Method	SCF	PNO-CI	CEPA-2	other calc.	experiment		
H ₂ CO	Basis	C		CNDO/2 ^a	CNDO/S ^b		
	α_x	11.34	11.37	11.54	4.45	12.35 ^c	
	α_y	15.68	15.92		15.45	8.03	18.63
	α_z	20.24	20.47		28.88	23.42	18.63
	$\bar{\alpha}$	15.75	15.92		18.63	11.95	16.53
H ₂ CS	Basis	B	B				
	α_x	21.12	20.91	B			
	α_y	24.12	24.21	24.25			
	α_z	41.85	41.05	39.94			
	$\bar{\alpha}$	29.03	28.72	28.30			
H ₂ O	Basis	B	B	B			
	α_x	3.90	4.02	7.45	SCF ^d	CEPA-1 ^d	
	α_y	7.30	7.49	9.45	7.99	9.59	
	α_z	5.70	5.86	8.44	9.04	9.81	
	$\bar{\alpha}$	5.63	5.79	8.45	8.47	9.64	9.82 ^e
CO	Basis	B	B	B			
	$\bar{\alpha}$	9.93	10.12	12.50	SCF ^d	CEPA-1 ^d	
	α_{\perp}	8.24	8.24	11.23	12.40	13.13	13.08 ^f
	α_{\parallel}	13.30	13.89	15.04			10.97
	$\alpha_{\parallel} - \alpha_{\perp}$	5.06	5.65	3.81	3.19	3.91	17.55

^a Ref. [62].

^b Ref. [61].

^c Ref. [46], at $\lambda = 5893 \text{ \AA}$.

^d Ref. [25] (with a larger basis than our basis D or E).

^e Ref. [44].

^f Ref. [53].

^g Ref. [54], Ref. [55].

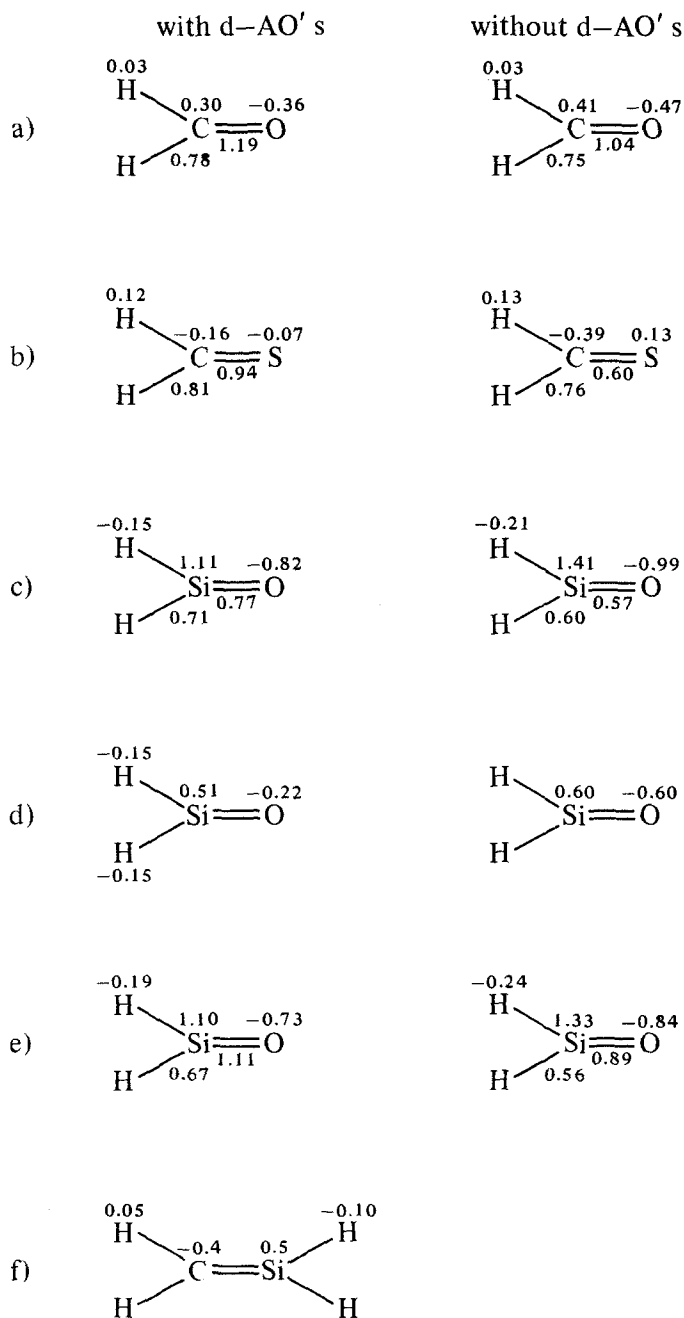


Fig. 3. Gross charges and overlap populations, calculated with and without *d*-AO's: a) H₂CO, b) H₂CS, c) H₂SiO, d) H₂SiO, with *d*-AO's, σ and π -contributions separately, e) H₂SiO, without flat *s* and *p*-AO's at O, f) H₂CSiH₂ (Ref. [14]) for comparison

Experimental values for the polarizability are very scarce, such that in spite of the rather large errors in theoretical values they may serve as useful estimates when no data are available.

7. Population Analysis and Role of the *d*-AO's

The Mulliken [26] gross and overlap populations give some insight into the bonding situation in molecules. Although the actual values of these populations depend to some extent on the chosen basis and should hence not be taken too literally, differences between different molecules obtained with comparable basis sets, are usually meaningful.

On Fig. 3 molecular diagrams based on the total gross populations, and the overlap populations for the bonds are given for H₂CO, H₂CS and H₂SiO.

The difference in the effective charges is significant. The CO bond is quite polar, the CS bond nearly unpolar, whereas the SiO bond with the charge transfer of nearly one electron is highly polar. The higher polarity of the CH bond in H₂CS as compared to that in H₂CO is probably responsible for the higher bond strength.

The overlap population of the X=Y bonds decreases in the order CO, CS, SiO which indicates decreasing double bond character.

The populations of *d*-AO's are given in Table 11.

One sees that they are very small, and only for Si in H₂SiO of the same order of magnitude as for P in the "hypervalent" H₃PO [6]. Even for Si the *d*-AO's cannot be regarded as valence-AO's. They rather serve to deform the *p*-AO's.

Inclusion of *d*-AO's reduces the polarity of the XY bond and increases its overlap population. This effect is most spectacular in H₂CS.

We have already mentioned that for an appropriate description of H₂SiO "flat" *s* and *p* functions on O have to be included. These additional functions serve to stabilize the negative charge on O, and in fact they increase the polarity of the SiO bond and reduce the overlap population, i.e. they make the bond more ionic. In the population analysis quoted in this section these flat functions were included for H₂SiO, i.e. basis B was used for H₂SiO, but basis A for H₂CO and H₂CS.

One sees from Fig. 3 that the π and the σ -bond in H₂SiO give roughly the same contribution to the polarity of the molecule.

The SiC bond in H₂CSiH₂ has been described as highly polar [14], but the charge transfer from Si to C is only about half as large as in H₂SiO.

Table 11. Population of *d*-AO's in H₂XY

	X	Y
H ₂ CO ^a	0.105	0.020
H ₂ CS ^a	0.045	0.077
H ₂ SiO ^b	0.234	0.012
H ₂ SiO ^a	0.224	0.013
H ₃ PO ^c	0.30	0.05

^a Basis A, i.e. without flat *s* and *p*-AO's on O.

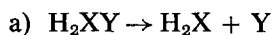
^b Basis B, i.e. with flat *s* and *p*-AO's on O.

^c Ref. [6].

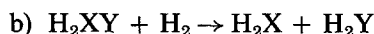
8. Orbital Energies and Binding Energies

The orbital energies and the total energies from the calculations with the most extended basis sets for H_2CO , H_2CS and H_2SiO at geometries close to the equilibrium are given in Table 12. This table is self-explanatory.

In order to get an estimate for the strength of the XY bond we have calculated the energy of the two reactions (consistently with basis set A)



with all species in their respective ground states. Since correlation effects which contribute considerably to the energy of this reaction are not sufficiently well described by basis A this estimate is expected to yield too small bond dissociation energies.



with all species in their lowest closed-shell singlet states. From known values [48] for the heats of formation of H_2 , H_2X , H_2Y we get a second estimate for the bond dissociation energies.

Table 12a. Orbital Energies in Hartree

H_2CO basis B		H_2CS basis A		H_2SiO basis B	
$1a_1$	-20.5767	$1a_1$	-91.9379	$1a_1$	-68.8486
$2a_1$	-11.3448	$2a_1$	-11.3257	$2a_1$	-20.5670
$3a_1$	-1.4117	$3a_1$	-8.9441	$3a_1$	-6.1986
$4a_1$	-0.8640	$4a_1$	-6.6172	$4a_1$	-4.3013
$1b_2$	-0.6926	$1b_1$	-6.6156	$1b_1$	-4.2991
$5a_1$	-0.6530	$1b_2$	-6.6136	$1b_2$	-4.2980
$1b_1(\pi)$	-0.5387	$5a_1$	-1.0599	$5a_1$	-1.2688
$2b_2$	-0.4394	$6a_1$	-0.8072	$6a_1$	-0.7170
		$2b_2$	-0.6329	$2b_2$	-0.5556
		$7a_1$	-0.5295	$7a_1$	-0.5272
		$2b_1(\pi)$	-0.4091	$2b_1(\pi)$	-0.4577
		$3b_2$	-0.3413	$3b_2$	-0.4470
$r(\text{C—O}):1.199$		$r(\text{C—S}):1.611$		$r(\text{Si—O}):1.522$	
$r(\text{C—H}):1.115$		1.086		$r(\text{Si—H}):1.471$	
$\angle\text{HCH}:116.3$		115.2		$\angle\text{HSiH}:110.0$	

Table 12b. Total energies in Hartree

	H_2CO basis B	H_2CS basis A	H_2SiO basis B
SCF	-113.8982	-436.4011	-364.7344
IEPA	-114.3146	-436.7446	-365.1432
CEPA	-114.2365	-436.6964	-365.0743
CI	-114.2077	-436.6575	-365.0502

Taking into account corrections for zero-point vibrations we obtain the following XY bond dissociation energies (in kcal/mol)

	computed		experimental	
	method a)	method b)	[47]	[60]
H ₂ CO	150	193	173 ± 6	172 ± 3
H ₂ CS	104	139	124 ± 7	129 ± 5
H ₂ SiO	118	155	—	—

From this we predict a value of 140 ± 5 kcal/mol for H₂SiO. This is much smaller than the dissociation energy of the SiO molecule (192.2 kcal/mol [27]), but larger than what one might expect for a SiO single bond (80–90 kcal/mol [28]) and even larger than the SiO bonding energy in quartz (~ 119 kcal/mol).

A π -contribution to the SiO binding energy in Me₂SiO has been estimated [29] as > 38 kcal/mol. This is consistent with our results for the total SiO bonding energy and current estimates for the energy of a single SiO bond. Ahlrichs and Heinzmann [14] have computed the rotational barrier of H₂C=SiH₂ as ~ 46 kcal/mol and proposed to regard this value as a measure of the π -binding energy in H₂C=SiH₂. The order of magnitude of the π -binding energy of the Si=C bond is hence the

Table 13. Contributions of the various valence shell pairs to the IEPA correlation energy (negative, in Hartree)^a

	C ₂ H ₄ ^b	H ₂ CO basis A	H ₂ CS basis A	H ₂ SiO basis B
<i>cc</i>	0.02511	0.02716	0.02290	0.02398
<i>hh</i>	0.03006	0.03147	0.03044	0.02935
<i>nn</i>	—	0.02166	0.02175	0.02204
¹ <i>ch</i>	0.00527	0.00381	0.00527	0.00102
¹ <i>cn</i>	—	0.01014	0.00594	0.01241
¹ <i>cc'</i>	0.01510	0.01655	0.01376	0.01423
¹ <i>hn</i>	—	0.00084	0.00061	0.00038
¹ <i>hn'</i>	—	0.00103	0.00073	0.00070
¹ <i>hh'</i>	—	0.00599	0.00594	0.00233
¹ <i>nn'</i>	—	0.01039	0.00846	0.01096
³ <i>ch</i>	0.00865	0.00639	0.00844	0.00202
³ <i>cn</i>	—	0.01548	0.00995	0.01790
³ <i>cc'</i>	0.01932	0.02360	0.01882	0.02103
³ <i>hn</i>	—	0.00121	0.00103	0.00068
³ <i>hn'</i>	—	0.00155	0.00139	0.00095
³ <i>hh'</i>	—	0.00894	0.00910	0.00371
³ <i>nn'</i>	—	0.01459	0.01136	0.01634

^a The abbreviations for the localized orbitals mean: *c* = CC, CO, CS or SiO banana bond, *h* = CH bond, *n* = lone pair, ¹*xy* means that the pair *xy* is coupled to a singlet, ³*xy* to a triplet. For geometries see Table 12.

^b Ref. [9].

	H ₂ CO	H ₂ CS	H ₂ SiO
<i>cc</i> , ¹ <i>cc'</i>	-0.00189	-0.00167	—
<i>cc</i> , ³ <i>cn</i>	0.00215	0.00103	0.00273
<i>cc</i> , ³ <i>cc'</i>	0.00385	0.00309	0.00340
<i>cc</i> , ³ <i>ch</i>	—	0.00106	—
<i>hh</i> , ³ <i>hh'</i>	0.00109	0.00104	—
<i>hh</i> , ³ <i>ch</i>	—	0.00100	—
<i>nn</i> , ³ <i>cn</i>	0.00144	0.00110	0.00219
<i>nn</i> , ³ <i>nn'</i>	0.00135	0.00131	0.00186
<i>nn</i> , ¹ <i>nn'</i>	—	0.00165	—
³ <i>nn'</i> , ³ <i>cn</i>	0.00122	—	0.00180
³ <i>cn</i> , ³ <i>c'n</i>	0.00228	0.00150	0.00256
³ <i>cn</i> , ³ <i>cn'</i>	0.00141	—	0.00209
³ <i>cc'</i> , ³ <i>cn</i>	0.00186	0.00118	0.00228
³ <i>cn</i> , ¹ <i>cn</i>	0.00160	—	0.00239
³ <i>ch</i> , ¹ <i>ch</i>	—	0.00100	—
³ <i>cc'</i> , ¹ <i>cc'</i>	0.00420	0.00318	0.00359
³ <i>hh'</i> , ¹ <i>hh'</i>	0.00107	0.00105	—
³ <i>nn'</i> , ¹ <i>nn'</i>	0.00129	0.00121	0.00170
³ <i>cn</i> , ¹ <i>cc'</i>	—	—	0.00113
³ <i>cc'</i> , ¹ <i>cn</i>	—	—	0.00111
³ <i>cn</i> , ¹ <i>c'n</i>	—	—	0.00106

Table 14. Pair coupling terms $\Delta\epsilon_{\mu\nu}$, which satisfy $|\Delta\epsilon_{\mu\nu}| \geq 0.001$ a.u.^a

^a As to the notation of the pairs see the footnote to Table 13.

same as for the Si=O bond. It is hence not astonishing that either bond has a strong tendency to polymerize (or oligomerize) i.e. to form two single SiC (or SiO) bonds rather than one double bond.

9. Analysis of the Contributions to the Correlation Energy

In a previous series of papers we have analyzed the different contributions to the correlation energy for some small molecules [7–9], a similar analysis for H₂CO, H₂CS and H₂SiO is complementary.

In Table 13 we give the contributions of the different pairs in a localized representation of the three H₂XY molecules together with the corresponding values for ethylene. As one expects, the contributions of similar pairs are quite comparable, although even the CH bonds differ somewhat. Table 13 confirms the trends, observed previously [7, 8] concerning differences in first and second row elements. Complementary to Table 13 the most important pair coupling terms are given in Table 14. One sees that the number of relevant pair coupling terms is relatively small and that all these pairs are either fully joint or semijoint (for the notation see Ref. [11]) and refer to the coupling of pairs that have at least one atom in common. With one exception all the coupling terms (between localized pairs) are positive.

10. Conclusions

We have confirmed in this study that with standard basis sets including the necessary polarization functions, equilibrium distances can be obtained on CEPA level with

an error of a few thousands on an Å and that comparison with experiment is only meaningful if one compares r_e with r_e -geometries.

As far as harmonic force constants are concerned no serious problems seem to exist on CEPA level for stretching of single bonds and for bending, whereas for double- and triple-bond stretch the inclusion of singly substituted configurations is necessary. Off-diagonal force constants from theory are probably more reliable than those from experiment. The comparison of theoretical and experimental harmonic frequencies is hence more significant than that of the force constants. Correlation has little effect on the second derivative of the energy, such that one nearly obtains the correct force constants if one differentiates twice the SCF energy at the CEPA or the experimental geometry.

The CH bond is significantly stronger in H₂CS than in H₂CO.

The calculation of dipole moments requires rather large basis sets (at least two sets of polarization functions) and the inclusion of singly substituted configurations. The CEPA-results differ then from experiment by ~0.1 Debye and are significantly better than SCF results, while PNO-CI agrees somewhat better with experiment for H₂CO and CO.

Dipole polarizabilities require still larger basis sets (three sets of polarization functions) but are not very sensitive to correlation effects.

In H₂SiO the O atom carries such a large negative charge that flat *s* and *p*-AO's on O are necessary. The population of the *d*-AO's is small in all molecules studied. It is largest on Si in H₂SiO, but even there the *d*-AO's are "polarization functions" in the proper sense and not valence-AO's, much like in H₃PO.

We predict a binding energy of 140 ± 5 kcal/mol for H₂SiO with respect to H₂Si (¹A₁) + O (³P).

The pair contributions to the correlation energy are consistent with previous analyses, especially as far as differences between first and second-row elements are concerned.

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