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Ab initio SCF Computation of Force Constants for CO_2

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Force constants for CO_2 have been evaluated using SCF wave functions. The effect of *d* basis functions and geometry are investigated. Comparison with experimental values shows that a large error, due to neglect of electron correlation, occurs for the K_{12} interaction stretch force constant.

Key word: CO_2, force constants of ~

1. Introduction

Ab initio SCF computations of force constants have been performed on a variety of polyatomic molecules [1–4]. Here, we report the computation of force constants at the SCF level for the CO_2 molecule utilizing a large Gaussian basis set, with and without *d* functions, and compare our results with an earlier computation for CO_2 [3]. An analysis is also presented for the *ab initio* force constants computed at the experimental equilibrium geometry.

2. Method of Computation and Results

The force constants are computed by a Taylor series expansion about the equilibrium geometry as shown below for CO_2.

$$E=E_0+\sum_{i=1}^{3} K_i\Delta R_i+\sum_{i\leq j=1}^{3} K_{ij}\Delta R_i\Delta R_j + \sum_{i\leq j\leq k=1}^{3} K_{ijk}\Delta R_i\Delta R_j\Delta R_k+\sum_{i\leq j\leq k\leq l=1}^{3} K_{ijkl}\Delta R_i\Delta R_j\Delta R_k\Delta R_l; \quad (1)$$

When E is expanded about the computed equilibrium geometry, the linear terms, K_i, are zero. K_{ij}, K_{ijk}, K_{ijkl} are the quadratic, cubic and quartic force constants, and the ΔR_i are the internal coordinates, ΔR_1, ΔR_2 are the two CO bond stretches and ΔR_3 is the change in bond angle. By symmetry, the quadratic force constants K_{11}, K_{22} are equal. K_{33} is the bending force constant and K_{12} is the stretch-stretch interaction force constant.

To determine all the force constants in Eq.(1) would require computing the energy as a function of both CO bond lengths and bond angles simultaneously.

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This would mean that the SCF energy would have to be calculated for many points and thus would require a large amount of computational time. We chose instead to compute the energy as a function of bond lengths with the nuclei fixed in a linear configuration; and, in separate series of calculations to compute the energy as a function of bond angle with the bond lengths fixed at the computed equilibrium values. In this manner all stretching and bending force constants may be computed to quartic terms, but no stretch bend interaction terms are obtained. However, this is not a serious limitation since quadratic stretch-bend interaction terms are zero by symmetry.

The calculations reported here were carried out with a Gaussian basis set taken from van Duijneveldt [5]. His elementary Gaussian basis set of $(12s,7p)$ functions was contracted to $\langle 5s,3p \rangle$ contracted Gaussian functions, CGTO's. An SCF potential surface, as described above, was obtained with this basis set. A single d polarization function, as determined by Roos and Siegbahn [6], was then added on both carbon and oxygen to form a $\langle 5s,3p,1d \rangle$ CGTO set. A second SCF potential surface was obtained for this basis set. The Gaussian basis

Table 1. The Gaussian basis set exponents and contraction coefficients used for carbon. The s and p exponents are taken from van Duijneveldt, Ref. [5], and the d exponent from Roos and Siegbahn, Ref. [6]

Type		Exponent	Contraction Coefficient
s	1	27736.6	0.000117
		4143.52	0.000912
		939.514	0.004787
		264.795	0.019857
		85.7790	0.067684
		30.6674	0.18212
	2	11.8181	0.349353
		4.86688	0.377588
		2.096688	0.14624
	3	0.678103	1.0
	4	0.262973	1.0
	5	0.102594	1.0
p	1	51.7233	0.002734
		12.3397	0.018979
		3.77224	0.08081
		1.32387	0.227778
	2	0.505457	0.388471
		0.198268	0.384051
	3	0.077314	1.0
d	1	0.63	1.0

Table 2. The Gaussian basis set exponents and contraction coefficients used for oxygen. The *s* and *p* exponents are taken from van Duijneveldt, Ref. [5], and the *d* exponent from Roos and Siegbahn, Ref. [6]

Type		Exponent	Contraction Coefficient
s	1	57134.2	0.000099
		8526.18	0.00077
		1929.08	0.004064
		542.47	0.016952
		176.046	0.058127
		63.3212	0.160039
	2	24.6143	0.322624
		10.2175	0.38923
		4.38355	0.189681
	3	1.40821	1.0
	4	0.548532	1.0
	5	0.206187	1.0
p	1	114.863	0.002266
		26.8767	0.017192
		8.32077	0.075343
		2.97237	0.212776
	2	1.12848	0.370484
		0.423603	0.39851
	3	0.15074	1.0
d	1	1.33	1.0

set exponents and contraction coefficients used for carbon and oxygen are shown in Tables 1 and 2.

All calculations were performed using the joint MOLECULE/ALCHEMY SCF program[1].

The SCF energy surface was constructed for the linear geometry by computing the energy at different carbon-oxygen bond distances. The results for the basis set without *d* functions are shown in Table 3. The results for the basis set with *d* functions are shown in Table 4.

Each energy surface was fit to quartic, cubic and quadratic equations by the least squares method. In the cubic and quartic fits all of the computed points were included in the least squares analysis. In the quadratic fit, only nine points closest

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[1] The joint MOLECULE-ALCHEMY program package incorporates the MOLECULE integral program and the ALCHEMY SCF program. MOLECULE was written by Dr. J. Almlöf of the University of Uppsala, Sweden. The ALCHEMY SCF program was written by Drs. P. S. Bagus and B. Liu of the IBM San José Research Laboratory. The interfacing of these programs was performed by Drs. U. Wahlgren (presently at the University of Uppsala) and P. S. Bagus at IBM [7].

Table 3. The linear CO_2 SCF potential surface for the basis set without polarization functions; $\langle 5s,3p \rangle$ CGTO's on carbon and oxygen. The bond distances are given so that $r(CO_a) \geqslant r(CO_b)$. Lengths and energies are in atomic units, Bohrs and Hartrees, respectively

$r(CO_a)$	$r(CO_b)$	$E_{SCF}+187$
2.304	2.304	−0.533 633 92
	2.254	−0.537 424 56
	2.204	−0.539 232 36
	2.154	−0.538 613 93
	2.104	−0.535 060 84
2.279	2.204	−0.541 030 40
2.254	2.254	−0.540 896 95
	2.229	−0.541 913 65
	2.204	−0.542 380 48
	2.179	−0.542 240 24
	2.154	−0.541 431 57
	2.104	−0.537 541 57
2.237	2.237	−0.542 356 26
2.229	2.204	−0.543 232 50
	2.179	−0.543 008 60
	2.154	−0.542 115 43
2.225	2.225	−0.543 046 13
2.218	2.204[a]	−0.543 435 91
	2.190[a]	−0.543 368 51
2.213	2.213[a]	−0.543 439 78
2.204	2.204[a]	−0.543 532 86
	2.190[a]	−0.543 438 95
	2.179	−0.543 224 38
	2.154	−0.542 245 72
	2.129	−0.540 531 15
	2.104	−0.538 010 07
2.190	2.190[a]	−0.543 318 33
2.179	2.154	−0.541 765 12
2.174	2.174	−0.542 512 24
2.162	2.162	−0.541 495 16
2.154	2.154	−0.540 612 26
	2.104	−0.536 022 15
2.104	2.104	−0.531 068 44

[a] Points nearest the computed equilibrium and used for the quadratic polynomial fit as described in the text.

Table 4. The linear CO_2 SCF potential surface for the basis set with polarization functions; $\langle 5s,3p,1d \rangle$ CGTO's on carbon and oxygen. For units and notation see Table 3

$r(CO_a)$	$r(CO_b)$	$E_{SCF}+187$
2.237	2.237	−0.674 149 93
	2.150	−0.679 443 67
	2.067	−0.675 937 99
2.195	2.190	−0.681 226 91
2.190	2.170	−0.682 329 00
	2.150	−0.682 703 87
	2.130	−0.682 594 47
	2.110	−0.681 960 51
2.187	2.187	−0.681 801 45
2.172	2.172	−0.682 981 85
2.170	2.150[a]	−0.683 416 01
	2.130	−0.683 248 03
	2.110	−0.682 554 71
2.160	2.140[a]	−0.683 569 39
2.157	2.157[a]	−0.683 594 10
2.150	2.150[a]	−0.683 676 45
	2.130[a]	−0.683 449 09
	2.110	−0.682 695 57
	2.067	−0.679 100 77
2.137	2.137[a]	−0.683 471 25
2.130	2.130	−0.683 161 51
	2.110	−0.682 346 98
2.118	2.118	−0.682 293 47
2.100	2.100	−0.680 157 37
2.067	2.067	−0.673 442 67

[a] See footnote to Table 3.

to and symmetrically located around the minimum were used; these points are denoted by "a" in Tables 3 and 4. The results for each fit are shown in Table 5 for the basis set without *d* functions, while Table 6 shows the results for the basis with *d* functions. The results for the SCF energy surface as a function of bond angle with fixed bond lengths for both basis sets are shown in Table 7. The force constants obtained by quartic and quadratic fits to each surface are also shown in Table 7. In all cases, the force constants are evaluated at the appropriate computed equilibrium geometry.

Tables 5, 6, and 7 show that for each basis set the quartic, cubic and quadratic fits give the same computed equilibrium geometry and essentially identical force constants. Thus, our computed surface is adequately described by the fitted polynomials.

Vucelić *et al.* [3] have obtained an SCF potential surface for CO_2 using a smaller, double zeta, $\langle 4s,2p\rangle$ CGTO basis set. They obtain an equilibrium

Table 5. Stretching mode force constants[a] for the $\langle 5s,3p\rangle$ SCF potential surface of linear CO_2. The force constants are determined by fitting quadratic, cubic, and quartic polynomials to the calculated surface. Geometry, r_e(CO), and energy are given for the fitted, $D_{\infty h}$, minimum

Force Constant	Degree of Polynomial Fit		
	Quartic	Cubic	Quadratic
$K_{11} \equiv K_{22}$	0.487	0.492	0.488
K_{12}	0.135	0.135	0.137
$K_{111} \equiv K_{222}$	−0.635	−0.636	
$K_{112} \equiv K_{221}$	−0.030	−0.030	
$K_{1111} \equiv K_{2222}$	0.434		
$K_{1112} \equiv K_{2221}$	0.0059		
K_{1122}	0.036		
r_e(CO)	2.204	2.204	2.204
Energy	−187.54343292	−187.54343999	−187.54343286

[a] K_{11}, K_{12} in units of Hartrees/Bohr^2; K_{111}, K_{112} in units of Hartrees/Bohr^3; K_{1111}, K_{1112}, K_{1122} in units of Hartrees/Bohr^4; r_e in units of Bohr; Energy in Hartrees.

Table 6. Stretching mode force constants for the $\langle 5s,3p,1d\rangle$ SCF potential surface of linear CO_2. See Table 5 for definitions and units

Force Constant	Degree of Polynomial Fit		
	Quartic Fit	Cubic Fit	Quadratic Fit
$K_{11} \equiv K_{22}$	0.611	0.616	0.606
K_{12}	0.149	0.149	0.142
$K_{111} \equiv K_{222}$	−0.779	−0.773	
$K_{112} \equiv K_{221}$	−0.050	−0.050	
$K_{1111} \equiv K_{2222}$	0.554		
$K_{1112} \equiv K_{2221}$	0.0088		
K_{1122}	0.032		
r_e(CO)	2.149	2.149	2.149
Energy	−187.68367742	−187.68368248	−187.68367613

Table 7. SCF energy surface as a function of bond angle and force constants for the bending mode of $CO_2(C_{2v}$ symmetry)

Bond Angle (degrees)	$E_{SCF}+187.0$ (Hartrees)			
	Without Polarization Functions $\langle 5s,3p \rangle$		With Polarization Functions $\langle 5s,3p,1d \rangle$	
180	−0.543 532 92[a]		−0.683 677 42[a]	
178	−0.543 437 37		−0.683 540 46	
176	−0.543 150 08		−0.683 129 11	
174	−0.542 668 96		−0.682 441 77	
172	−0.541 991 66		−0.681 475 88	
	$r_e(CO)=2.204$		$r_e(CO)=2.149$	
	Quartic Fit	Quadratic Fit	Quartic Fit	Quadratic Fit
K_{33}[b]	0.078	0.079	0.112	0.113
K_{3333}[c]	0.033	—	0.029	—

[a] Energies obtained as minima of quartic fits to the linear surface rather than from direct SCF calculations.

[b] K_{33} in units of Hartrees/radian^2.

[c] K_{3333} in units of Hartrees/radian^4.

Table 8. Comparison of SCF energies for linear symmetric $(D_{\infty h})$ CO_2 for various basis sets

Basis Set	$r(CO)$ Bohrs		$E_{SCF}+187$ (Hartrees)
Vucelić *et al.*[a] CGTO	$\langle 4s,2p \rangle$	2.190	−0.306 420
	$\langle 4s,2p,1d \rangle$	2.190	−0.446 723
Present Work CGTO	$\langle 5s,3p \rangle$	2.204	−0.543 533
	$\langle 5s,3p,1d \rangle$	2.149	−0.683 677
McLean and Yoshimine[b] STO	$(5s,4p,1d,1f)$	2.1444	−0.725 36

[a] See Ref. [3].

[b] See Ref. [8].

$r_e(CO)=2.190$ Bohrs. At this point they obtained an SCF energy for a $\langle 4s,2p,1d \rangle$ basis set. In Table 8 we compare our computed energies at the point nearest the computed $r_e(CO)$ with Vucelić *et al.*'s [3] values. We also include the near Hartree-Fock energy obtained by McLean and Yoshimine [8] who used a $(5s,4p,1d,1f)$ Slater (STO) basis set. McLean and Yoshimine estimate that their results are within 0.002 Hartrees of the Hartree-Fock limit. The energy given in Table 8 is for $r(CO)=2.1444$ Bohrs and is the lowest energy obtained by them. We note that our total energies are ~0.24 Hartrees or ~7 eV below the values (both with and without d functions) obtained by Vucelić *et al.* [3]. However comparison with the results of McLean and Yoshimine [8] shows we are still ~0.04 Hartrees or ~1.1 eV from the Hartree-Fock limit.

3. Discussion

In Table 9, we present our results for the CO_2 force constants (as obtained from the quartic polynomial fits), and the results of Vucelić *et al.* [3] for the quadratic constants. The values obtained from analysis of experimental vibrational energies [9, 10] are also given. The stretch mode force constants have been evaluated at both the calculated r_e(CO), appropriate for each level of calculation, and the experimental $r_e(\mathrm{CO}) = 2.192$ Bohrs [11]. For the latter case, the force constants are obtained by evaluating the appropriate derivatives of Eq.(1) at the experimental r_e. We discuss first the case where the force constants have been evaluated at the computed r_e.

The equilibrium geometry obtained with our $\langle 5s,3p \rangle$ basis and that obtained by Vucelić *et al.* [3] are essentially the same and in close agreement with the experimental r_e. However, the quadratic force constants are rather different.

In comparison of the quadratic force constants for the stretching modes obtained with different basis sets, it is seen that inclusion of *d* functions into the basis set decreases the equilibrium bond lengths and has the concomitant effect of increasing the magnitude of the force constants over those computed without *d* functions. The same situation exists for the cubic force constants and the quartic force constants K_{1111} and K_{1112}. The bending force constant K_{33} is also shifted to a higher value when *d* functions are included in the basis set.

Contrasting our results for the basis set without *d* functions and those obtained experimentally shows that except for K_{12} and K_{3333}, all of the computed force constants have lower values. On the other hand, a comparison of our results for the basis with *d* functions and experiment shows that the computed equilibrium geometry is shorter than experiment and the computed force constants are in general much higher than the experimental values.

We thus conclude that force constants are clearly basis set dependent quantities and that care must be exercised in the selection of a proper basis set.

Schwendeman [12] has shown that errors in the computed equilibrium geometry can lead to first-order errors in the derivatives of the energy and hence in the force constants. As a consequence, he has suggested that force constants be determined using derivatives of the energy evaluated at or near the experimental equilibrium geometry. We have done this for the stretch mode constants and the results are given in Table 9. The values for the two basis sets, with and without *d* functions, are much closer to each other in this case. In particular, the very large difference between the values of K_{11} has been greatly reduced and K_{11} is now in quite good agreement with experiment [10, 11]. However, significant errors remain in the force constants; the error of K_{12} is 74% with *d* functions and 69% without *d* functions. (Since the force constants have been obtained using quartic polynomial fits, it is obvious that the value of the quartic constants (K_{1111}, K_{1112}, and K_{1122}) must be the same whether they are evaluated at the computed or experimental geometry.)

If the force constants are evaluated at the calculated r_e, we find that their values are strongly dependent on the basis set used for the calculation. However, if Schwendeman's procedure is followed and the constants are computed at the

Table 9. Force constants for CO_2 from computed SCF potential surfaces and experimentally observed vibrational levels. Subscripts 1 and 2 are for the CO bonds and 3 is for the CO_2 bond angle. The numbers in parentheses after the computed force constants are the errors with respect to the experimental values of Ref. [10]

		$\langle 4s,2p \rangle$ Basis Set Vucelić *et al.*[a]	$\langle 5s,3p \rangle$ Basis Set This Work	$\langle 5s,3p \rangle$ Basis Set[b] This Work; Exp. Geo.	$\langle 5s,3p,1d \rangle$ Basis Set This Work	$\langle 5s,3p,1d \rangle$ Basis Set[b] This Work; Exp. Geo.	"Experiment"[c]	"Experiment"[e]
mdyn/Å	K_{11}	8.54(7%)	7.59(−5%)	7.94	9.52(19%)	8.02	8.011±0.002	8.015
	K_{12}	1.92(52%)	2.11(67%)	2.13	2.31(83%)	2.19	1.261±0.004	1.252
mdyn.Å/(rad)^2	K_{33}	0.30(−24%)	0.34(−13%)		0.49(25%)		0.3925±0.0002	0.3913
mdyn/Å^2	K_{111}	–	−18.69(−2%)	−19.29	−22.93(21%)	−20.12	−18.99±0.03	−18.86
	K_{112}	–	−0.89(−54%)	−0.92	−1.47(−25%)	−1.36	−1.95±0.10	−0.821
mdyn/Å^3	K_{1111}	–	24.14(−8%)	24.14	30.82(17%)	30.82	26.25±0.17	25.27
	K_{1112}	–	0.35 (−91%)	0.35	0.49(−87%)	0.49	3.68±0.21	−1.08
	K_{1122}	–	1.98(−34%)	1.98	1.78(−41%)	1.78	3.02±0.40	−2.24
mdyn.Å/(rad)^4	K_{3333}	–	0.14(210%)		0.13(175%)		0.046±0.002	0.051
Å	r_e(CO)	1.159	1.166		1.137		1.160[d]	

[a] See Ref. [3].

[b] Force constants computed at experimental geometry; $r_e = 1.160$.

[c] See Ref. [9]. Values after ± are uncertainties for the "experimental" values.

[d] See Ref. [11].

[e] See Ref. [10].

experimental equilibrium geometry, the effect of the use of polarization functions is much smaller. This is consistent with the results of studies of CH_4 [13], NH_3 [14], and H_2CO [15]. However, even in this case there are significant errors in certain of the force constants, in particular K_{12}. Clearly, electron correlation effects must be considered in order to obtain more accuracy. A simple rule of thumb that Hartree-Fock force constants are accurate to about 10% does not apply for CO_2.

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