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Quadrupole polarizability and hyperpolarizability of carbon monoxide

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Summary. We report a study of the electric dipole-quadrupole ($A_{\alpha,\beta\gamma}$), quadrupole-quadrupole ($C_{\alpha\beta,\gamma\delta}$), dipole-octopole ($E_{\alpha,\beta\gamma\delta}$) polarizability and the dipole-dipole-quadrupole ($B_{\alpha\beta,\gamma\delta}$) hyperpolarizability of carbon monoxide. All values are obtained from finite-field self-consistent field (SCF) and fourth-order many-body perturbation theory (MP4) calculations. Our best values for the dipole-octopole polarizability are $E_{z,zzz} = 60.19$ and $E_{x,xxx} = -38.06\ e^2a_0{}^4E_h{}^{-1}$. For the dipole-dipole-quadrupole hyperpolarizability we report $B_{zz,zz} = -296$, $B_{xz,xz} = -170$, $B_{xx,zz} = 88$ and $B_{xx,xx} = -178\ e^3a_0{}^4E_h{}^{-2}$.

Key words: Carbon monoxide – Quadrupole polarizability – Quadrupole hyperpolarizability

1. Introduction

Few theoretical values of the electric quadrupole polarizability and hyperpolarizability of carbon monoxide are available in the literature. McLean and Yoshimine [1] reported self-consistent field (SCF) values of the parallel components of the dipole-quadrupole ($A_{\alpha,\beta\gamma}$) and the quadrupole-quadrupole ($C_{\alpha\beta,\gamma\delta}$) polarizability and the dipole-dipole-quadrupole ($B_{\alpha\beta,\gamma\delta}$) hyperpolarizability. SCF and configuration interaction (CI) values of $A_{\alpha,\beta\gamma}$ were reported by Amos [2, 3]. Diercksen and Sadlej [4] reported fourth-order many-body perturbation theory (MP4) calculations of $C_{zz,zz}$ and $C_{xx,xx}$. Coupled-Hartree–Fock (CHF) values of $A_{\alpha,\beta\gamma}$, $C_{\alpha\beta,\gamma\delta}$ and $E_{\alpha,\beta\gamma\delta}$ can be extracted from the effective time-dependent CHF multipole spectra reported by Visser and Wormer [5]. Derivative Hartree–Fock (DHF) theory was used by Liu and Dykstra [6] and Dykstra, Liu and Malik [7] to calculate $A_{\alpha,\beta\gamma}$, $C_{\alpha\beta,\gamma\delta}$ and $B_{\alpha\beta,\gamma\delta}$. $C_{\alpha\beta,\gamma\delta}$ values calculated in the CCD + ST(CCD) approximation (coupled-cluster doubles corrected by fourth-order contributions from single and triple excitations computed with CCD amplitudes) were reported by Maroulis and Thakkar [8]. Last, a CHF value of the mean quadrupole-quadrupole polarizability was reported by Spackman [9].

In this paper we report a systematic study of $A_{\alpha,\beta\gamma}$, $C_{\alpha\beta,\gamma\delta}$, $E_{\alpha,\beta\gamma\delta}$ and $B_{\alpha\beta,\gamma\delta}$. The properties are extracted from MP4 calculations of the energy of the molecule perturbed by arrays of strategically placed distant point charges. A large, carefully optimized basis set of Gaussian-type functions (GTF) is employed in these calculations. Thus, we ensure that the respective SCF results are of near-Hartree–Fock quality. Further SCF calculations were performed with a very large basis set in order to support the above claim. To our knowledge, the correlated values of $E_{\alpha,\beta\gamma\delta}$ and $B_{\alpha\beta,\gamma\delta}$ are the first to appear in the literature.

Atomic units are used throughout this work. The relevant conversion factors to SI units are given in the Appendix.

2. Theory and computational strategy

The energy and the dipole, quadrupole and octopole moments of an uncharged molecule in a weak, general electrical field can be written as [10–12]:

$$\begin{aligned} E^p = E^0 &- \mu_\alpha F_\alpha - (1/3)\Theta_{\alpha\beta}F_{\alpha\beta} - (1/15)\Omega_{\alpha\beta\gamma}F_{\alpha\beta\gamma} \\ &- (1/105)\Phi_{\alpha\beta\gamma\delta}F_{\alpha\beta\gamma\delta} + \cdots \\ &- (1/2)\alpha_{\alpha\beta}F_\alpha F_\beta - (1/3)A_{\alpha,\beta\gamma}F_\alpha F_{\beta\gamma} - (1/6)C_{\alpha\beta,\gamma\delta}F_{\alpha\beta}F_{\gamma\delta} \\ &- (1/15)E_{\alpha,\beta\gamma\delta}F_\alpha F_{\beta\gamma\delta} + \cdots \\ &- (1/6)\beta_{\alpha\beta\gamma}F_\alpha F_\beta F_\gamma - (1/6)B_{\alpha\beta,\gamma\delta}F_\alpha F_\beta F_{\gamma\delta} + \cdots \\ &- (1/24)\gamma_{\alpha\beta\gamma\delta}F_\alpha F_\beta F_\gamma F_\delta + \cdots \end{aligned} \tag{1}$$

$$\begin{aligned} \mu_\alpha{}^p = \mu_\alpha &+ \alpha_{\alpha\beta}F_\beta + (1/3)A_{\alpha,\beta\gamma}F_{\beta\gamma} + (1/15)E_{\alpha,\beta\gamma\delta}F_{\beta\gamma\delta} \\ &+ (1/2)\beta_{\alpha\beta\gamma}F_\beta F_\gamma + (1/3)B_{\alpha\beta,\gamma\delta}F_\beta F_{\gamma\delta} \\ &+ (1/6)\gamma_{\alpha\beta\gamma\delta}F_\beta F_\gamma F_\delta + \cdots \end{aligned} \tag{2}$$

$$\Theta_{\alpha\beta}{}^p = \Theta_{\alpha\beta} + A_{\gamma,\alpha\beta}F_\gamma + C_{\alpha\beta,\gamma\delta}F_{\gamma\delta} + (1/2)B_{\gamma\delta,\alpha\beta}F_\gamma F_\delta + \cdots \tag{3}$$

$$\Omega_{\alpha\beta\gamma}{}^p = \Omega_{\alpha\beta\gamma} + E_{\delta,\alpha\beta\gamma}F_\delta + \cdots \tag{4}$$

where $F_\alpha, F_{\alpha\beta}, \ldots$ are the field, field gradient, etc. at the origin, E^0, μ_α, $\Theta_{\alpha\beta}$, $\Omega_{\alpha\beta\gamma}$, $\Phi_{\alpha\beta\gamma\delta}$ the energy and permanent moments of the free molecule, and $\alpha_{\alpha\beta}$, $\beta_{\alpha\beta\gamma}$, $A_{\alpha,\beta\gamma}$, $C_{\alpha\beta,\gamma\delta}$, $E_{\alpha,\beta\gamma\delta}$ and $B_{\alpha\beta,\gamma\delta}$ the molecular polarizabilities. The Greek suffixes denote Cartesian components and a repeated suffix implies summation over x, y and z.

For a linear molecule such as CO, $A_{\alpha,\beta\gamma}$ has two independent components, $C_{\alpha\beta,\gamma\delta}$ three, $E_{\alpha,\beta\gamma\delta}$ two and $B_{\alpha\beta,\gamma\delta}$ four [10, 12, 13]. With z as the molecular axis we calculate $A_{z,zz}$, $A_{x,zx}$, $C_{zz,zz}$, $C_{xz,xz}$, $C_{xx,xx}$, $E_{z,zzz}$, $E_{x,xxx}$, $B_{zz,zz}$, $B_{xz,xz}$, $B_{xx,zz}$ and $B_{xx,xx}$. The values of these components depend on the chosen origin [10, 11], in this work the centre of mass. In addition to the above components we also report isotropic and anisotropic ones for $C_{\alpha\beta,\gamma\delta}$, defined as:

$$\bar{C} = (C_{zz,zz} + 8C_{xz,xz} + 8C_{xx,xx})/10 \tag{5}$$

$$\Delta_1 C = 5C_{zz,zz} + 4C_{xz,xz} + 8C_{xx,xx} \tag{6}$$

$$\Delta_2 C = 2C_{zz,zz} - 4C_{xz,xz} + C_{xx,xx} \tag{7}$$

Another property of interest is the isotropic component of $B_{\alpha\beta,\gamma\delta}$ defined as:

$$\bar{B} = (2/15)(B_{zz,zz} + 4B_{xz,xz} + B_{xx,zz} + 4B_{xx,xx}) \tag{8}$$

Algebraic formulae for the calculation of $C_{\alpha\beta,\gamma\delta}$, $E_{\alpha,\beta\gamma\delta}$ or $B_{\alpha\beta,\gamma\delta}$ from the perturbed molecular energies have been given in earlier work [14–16]. We use strategically placed arrays of distant point charges to simulate weak quadrupolar or octopolar fields. We give here the formulae used for the dipole-quadrupole polarizability $A_{z,zz}$ and $A_{x,zx}$. We use the symbol G_{zz} to denote the presence of four charges $-32Q$, Q, Q and $-32Q$ placed at $-2R$, $-R$, R and $2R$ on the z or molecular axis. Let $E(G_{zz})$ be the energy of the molecule in this quadrupolar field. Let $E(F_z)$ be the energy of the molecule interacting with a homogeneous electric field along the z axis and $E(F_z, G_{zz})$ the energy when both the homogeneous and the quadrupolar field are present. From Eq. (1) we have:

$$E(F_z) = E^0 - \mu_z F_z - (1/2)\alpha_{zz} F_z^2 - (1/6)\beta_{zzz} F_z^3 - (1/24)\gamma_{zzzz} F_z^4 + \cdots \tag{9}$$

$$E(G_{zz}) = E^0 - 6\Theta_{zz}(Q/R^3) - 54C_{zz,zz}(Q^2/R^6) + \cdots \tag{10}$$

$$\begin{aligned} E(F_z, G_{zz}) = E^0 &- \mu_z F_z - (1/2)\alpha_{zz} F_z^2 - (1/6)\beta_{zzz} F_z^3 \\ &- (1/24)\gamma_{zzzz} F_z^4 \\ &- 6\Theta_{zz}(Q/R^3) - 54C_{zz,zz}(Q^2/R^6) \\ &- 6A_{z,zz} F_z (Q/R^3) - 3B_{zz,zz} F_z^2 (Q/R^3) + \cdots \end{aligned} \tag{11}$$

or

$$\begin{aligned} E(F_z, G_{zz}) = E^0 &+ (E(F_z) - E^0) + (E(G_{zz}) - E^0) \\ &- 6A_{z,zz} F_z (Q/R^3) - 3B_{zz,zz} F_z^2 (Q/R^3) + \cdots \end{aligned} \tag{12}$$

Now, let:

$$D(F_z, G_{zzz}) = E(F_z, G_{zz}) - E(F_z) - E(G_{zz}) + E^0$$

so that:

$$D(F_z, G_{zz}) = -6A_{z,zz} F_z (Q/R^3) - 3B_{zz,zz} F_z^2 (Q/R^3) + \cdots \tag{13}$$

and

$$\begin{aligned} A_{z,zz} \approx [(D(-F_z, G_{zz}) - D(F_z, G_{zz})) &- (D(-F_z, -G_{zz}) \\ &- D(F_z, -G_{zz}))]/(24F_z Q/R^3). \end{aligned} \tag{14}$$

In a similar way we obtain:

$$\begin{aligned} (1/4)A_{z,zz} F_z + A_{x,zx} F_x \approx [(D(&-F_x, -F_z, G_{xz}) - D(F_x, F_z, G_{xz})) \\ &- (D(-F_x, -F_x, -G_{xz}) - D(F_x, F_z, -G_{xz}))]/(24Q/R^3) \end{aligned} \tag{15}$$

From Eqs. (14)–(15) we obtain $A_{z,zz}$ and $A_{x,zx}$.

Electron correlation corrections to the SCF values of the molecular properties were obtained from MP4 calculations of the relevant perturbed energies. Excellent reviews of many-body perturbation theory are available [17–20]. We restrict our presentation to a few essential points. The MP4 approximation to the energy is written as:

$$\mathrm{MP4} = \mathrm{SCF} + \mathrm{D2} + \mathrm{D3} + \mathrm{S4} + \mathrm{D4} + \mathrm{T4} + \mathrm{Q4} + \mathrm{R4} \tag{16}$$

where S, D, T and Q are contributions from single, double, triple and quadruple substitutions from the zeroth order wave function and R4 the renormalization term. Lower order approximations are also considered and are defined as:

$$\mathrm{MP2} = \mathrm{SCF} + \mathrm{D2} \tag{17}$$

$$\mathrm{MP3} = \mathrm{MP2} + \mathrm{D3} \tag{18}$$

$$\begin{aligned} \text{DQ-MP4} &= \mathrm{MP3} + \mathrm{D4} + \mathrm{Q4} + \mathrm{R4} \\ &= \mathrm{MP3} + \mathrm{DQR4} \end{aligned} \tag{19}$$

$$\begin{aligned} \text{SDQ-MP4} &= \mathrm{MP3} + \mathrm{S4} + \mathrm{DQR4} \\ &= \mathrm{MP3} + \mathrm{SDQR4} \end{aligned} \tag{20}$$

By virtue of Eqs. (19)–(20) we adopt similar decompositions for all molecular properties computed in this work.

We have also obtained molecular polarizabilities from the induced multipole moments, Eqs. (2)–(4), a more economical way to calculate polarizabilities [21, 22].

3. Basis set selection and computational details

Two basis sets were used in the calculations reported in this work. The first, hereafter basis A, consists of $(11s7p4d2f)$, or 132 primitive GTF, contracted to $[6s4p4d2f]$, or 104 contracted GTF. This set contains five-membered d-GTF and seven-membered f-GTF. It represents an augmented version of a carefully optimized $(11s7p3d2f)$ $[6s4p3d2f]$ basis set, which was used in the CCD + ST(CCD) calculation of $C_{\alpha\beta,\gamma\delta}$ [8]. The additional GTF are tight d-GTF on C and O with exponents 2.228519 and 2.706063 (in units of a_0^{-2}), respectively.

We used an even larger basis set, $(13s9p5d2f)$ $[8s6p5d2f]$, hereafter basis B (consisting of 180 primitive GTF contracted to 152 CGTF). This set contains six-membered d-GTF and ten-membered f-GTF. It was built on the $[6s4p3d]$ part of the basis set used in previous work [8], or basis A with the tight d-GTF and the f-GTF deleted. On this $[6s4p3d]$ substrate the f-GTF on both C and O were reoptimized and their exponents were chosen to maximize the mean quadrupole polarizability $\bar{C}$. The optimal values are 0.15 for carbon and 0.1668 for oxygen. The resulting $[6s4p3d1f]$ set was augmented to $[8s6p5d2f]$ by the following GTF:

C: $s(0.004521, 0.001397), p(0.003715, 0.001185),$
$d(1.248985, 0.021694)$ and $f(0.45)$
O: $s(0.007904, 0.002394); p(0.005656, 0.001685),$
$d(1.516625, 0.026343)$ and $f(0.4668)$

The quality of basis B may be judged from the values of the electric multipole moments, $\mu_z = -0.10499\, ea_0$, $\Theta_{zz} = -1.52911\, ea_0^2$, $\Omega_{zzz} = 4.40801\, ea_0^3$ and $\Phi_{zzzz} = -10.70097\, ea_0^4$. The respective numerical Hartree–Fock values are $\mu_z = -0.104245\, ea_0$, $\Theta_{zz} = -1.53001\, ea_0^2$, $\Omega_{zzz} = 4.42239\, ea_0^3$ and $\Phi_{zzzz} = -10.6883\, ea_0^4$ [23]. Agreement is significantly better than 1% in all cases.

We used basis A to obtain SCF and correlated values for $A_{\alpha,\beta\gamma}$, $C_{\alpha\beta,\gamma\delta}$, $E_{\alpha,\beta\gamma\delta}$ and $B_{\alpha\beta,\gamma\delta}$. SCF values for the same properties were calculated with basis B.

The MP4 approximation adopted in this work is SDQ-MP4. The inclusion of the $T4$ terms results in a dramatic increase of the computational cost of the calculations. SDQ-MP4 provides reliable predictions of molecular polarizabilities [14, 16, 24, 25]. The two innermost orbitals were kept frozen in all calculations and excitations to the two highest virtual orbitals were not allowed.

The strength of the field in the correlated calculations was $F_x = F_z = 0.01\, e^{-1}a_0^{-1}E_h$. Weak field gradients were used in these calculations as, in absolute terms, $(Q/R^3) = 0.0002\, e^{-1}a_0^{-2}E_h$. The SCF values calculated with basis B were obtained from the multipole moments induced by very weak fields.

All optimizations were performed at the experimental equilibrium internuclear separation of 2.132221 a_0 [26].

GAUSSIAN 86 [27] was used in all calculations.

4. Results and discussion

SCF polarizabilities calculated with basis sets A and B are given in Table 1, along with previous results by other authors. SCF values of $A_{\alpha,\beta\gamma}$, $E_{\alpha,\beta\gamma\delta}$ and $B_{\alpha\beta,\gamma\delta}$ at three different bond lengths are given in Table 2. Electron correlation

Table 1. Basis set dependence of the quadrupole polarizabilities of carbon monoxide[a]. All values in atomic units

Property	*VW*[b]	*DLM*[c]	*MT*[d]	*MT*[e]	*MT*[f]	*M*[g]	*M*[h]
$A_{z,zz}$	−11.20	−11.51	−11.29	−11.5	−11.3	−11.46	−11.32
$A_{x,zx}$	−13.70	−13.89	−13.81	−13.7	−13.7	−13.91	−13.78
$C_{zz,zz}$	41.66	41.07	42.15	42.30	42.53	42.29	42.53
$C_{xz,xz}$	34.66	34.02	35.12	34.96	35.26	35.24	35.32
$C_{xx,xx}$	23.21	19.89	22.99	23.25	23.49	23.52	23.70
$\bar{C}$	50.46	47.23	50.70	50.80	51.25	51.24	51.47
$\Delta_1 C$	161.27	182.31	167.31	169.34	165.77	164.30	164.31
$\Delta_2 C$	−32.12	−34.05	−33.18	−31.99	−32.49	−32.88	−32.53
$E_{z,zzz}$	52.68		53.41	53.0	53.7	53.91	53.44
$E_{x,xxx}$	−35.85		−36.92	−36.1	−36.3	−36.31	−36.35
$B_{zz,zz}$		−226				−241	−237
$B_{xz,xz}$		−127				−133	−131
$B_{xx,zz}$		72				72	74
$B_{xx,xx}$		−131				−146	−146
$\bar{B}$		−158				−171	−169

[a] At the experimental internuclear separation of 2.132221 a_0

[b] Visser and Wormer [5]. Basis set [6*s*5*p*3*d*2*f*]

[c] Dykstra, Liu and Malik [7]. Basis set [7*s*5*p*3*d*]

[d] Maroulis and Thakkar [28]. Basis set [6*s*4*p*3*d*1*f*]. Exponents of the *d*-GTF: C(0.70, 0.219877, 0.069065) and O(0.85, 0.266993, 0.083865). For the *f*-GTF the exponents are C(0.121110) and O(0.169819)

[e] Maroulis and Thakkar [28]. Basis set [6*s*4*p*4*d*1*f*]. Exponents of the *d*-GTF: C(2.80, 0.70, 0.175, 0.04375) and O(3.40, 0.85, 0.2125, 0.053125). For the *f*-GTF the exponents are C(0.228365) and O(0.320310)

[f] Maroulis and Thakkar [28]. Basis set [6*s*4*p*4*d*1*f*]. The same as the previous one with the exception of the most diffuse *d*-GTF for which C(0.065625) and O(0.079687)

[g] Present investigation. Basis set *A*, [6*s*4*p*4*d*2*f*], 104 CGTF

[h] Present investigation. Basis set *B*, [8*s*6*p*5*d*2*f*], 152 CGTF

Table 2. Bond length dependence of the quadrupole polarizabilities of carbon monoxide. Basis set *A*. All values in atomic units

Property	1.932221	2.132221	2.332221
$A_{z,zz}$	-11.84	-11.42	-11.24
$A_{x,zx}$	-14.32	-13.87	-13.41
$E_{z,zzz}$	48.92	53.89	60.52
$E_{x,xxx}$	-33.72	-36.31	-39.38
$B_{zz,zz}$	-221	-239	-264
$B_{xz,xz}$	-125	-132	-146
$B_{xx,zz}$	67	72	83
$B_{xx,xx}$	-141	-145	-159
$\bar{B}$	-163	-170	-186

corrections to the SCF values of all properties and correlated values are given in Tables 3 and 4, respectively.

SCF results. We expect the SCF values calculated with basis set *B* to be close to the respective Hartree–Fock limits. In this basis set $A_{z,zz} = -11.32$ and $A_{x,zx} = -13.78\, e^2a_0{}^3E_h{}^{-1}$. From basis *A* we obtain $A_{z,zz} = -11.46$ and $A_{x,zx} = -13.91\, e^2a_0{}^3E_h{}^{-1}$. The difference is of the order of 1%. Very good agreement is observed with the values of Visser and Wormer [15], Dykstra, Liu and Malik [7] and Maroulis and Thakkar [28]. We mention also the SCF results of Amos [2], $A_{z,zz} = -11.20$ and $A_{x,zx} = -13.56\, e^2a_0{}^3E_h{}^{-1}$, calculated with a small, [5*s*4*p*2*d*] basis set. It is obvious that the dipole-quadrupole polarizability is not very sensitive to basis set quality.

Table 3. Electron correlation corrections to the quadrupole polarizabilities of carbon monoxide[a]. Basis set *A*

Property[b]	SCF	D2	D3	S4	D4	QR4	SDQ-MP4
$A_{z,zz}$	-11.46	-2.78	0.99	-0.39	-0.41	0.12	-13.92
$A_{x,zx}$	-13.91	-1.52	0.79	-0.32	-0.12	0.07	-15.01
$C_{zz,zz}$	42.29	5.11	-2.13	0.57	0.61	-0.20	46.25
$C_{xz,xz}$	35.24	3.20	-1.60	0.51	0.34	-0.10	37.61
$C_{xx,xx}$	23.52	2.69	-1.09	0.23	0.32	-0.16	25.51
$\bar{C}$	51.24	5.22	-2.36	0.65	0.59	-0.22	55.12
$\Delta_1 C$	164.30	16.88	-8.32	3.03	1.83	-0.15	177.57
$\Delta_2 C$	-32.88	0.10	1.03	-0.66	0.16	-0.18	-32.42
$E_{z,zzz}$	53.91	5.87	-1.52	1.42	0.46	0.05	60.19
$E_{x,xxx}$	-36.31	-2.13	1.26	-0.70	-0.13	-0.04	-38.06
$B_{zz,zz}$	-241	-66	26	-6	-12	3	-296
$B_{xz,xz}$	-133	-43	15	-4	-7	2	-170
$B_{xx,zz}$	72	21	-8	2	2	-2	88
$B_{xx,xx}$	-146	-40	14	-4	-5	3	-178
$\bar{B}$	-171	-50	18	-5	-8	3	-213

[a] At the experimental internuclear separation of 2.132221 a_0

[b] In atomic units

Table 4. Correlated values for the quadrupole polarizabilities of carbon monoxide[a]. Basis set A. All values in atomic units

Property	SCF	MP2	MP3	DQ-MP4	SDQ-MP4
$A_{z,zz}$	-11.46	-14.24	-13.25	-13.53	-13.92
$A_{x,xz}$	-13.91	-15.43	-14.64	-14.69	-15.01
$C_{zz,zz}$	42.29	47.40	45.27	45.68	46.25
$C_{xz,xz}$	32.24	38.44	36.85	37.10	37.61
$C_{xx,xx}$	23.52	26.20	25.11	25.28	25.51
$\bar{C}$	51.24	56.46	54.10	54.47	55.12
$\Delta_1 C$	164.30	181.18	172.86	174.54	177.57
$\Delta_2 C$	-32.88	-32.77	-31.74	-31.76	-32.42
$E_{z,zzz}$	53.91	59.78	58.26	58.77	60.19
$E_{x,xxx}$	-36.31	-38.44	-37.18	-37.35	-38.06
$B_{zz,zz}$	-241	-307	-282	-291	-296
$B_{xz,xz}$	-133	-176	-161	-166	-170
$B_{xx,zz}$	72	93	86	86	88
$B_{xx,xx}$	-146	-186	-172	-174	-178
$\bar{B}$	-171	-222	-204	-208	-213

[a] At the experimental internuclear separation of 2.132221 a_0

A detailed study of $C_{\alpha\beta,\gamma\delta}$ for carbon monoxide has been published by Maroulis and Thakkar [8] who obtained $C_{zz,zz} = 42.21$, $C_{xz,xz} = 35.24$, $C_{xx,xx} = 23.52$ and $\bar{C} = 51.23\, e^2 a_0^4 E_h^{-1}$ with a $[6s4p3d2f]$ basis set. Basis A, slightly larger than the aforementioned, gives $C_{zz,zz} = 42.29$, $C_{xz,xz} = 35.24$, $C_{xx,xx} = 23.52$ and $\bar{C} = 51.24\, e^2 a_0^4 E_h^{-1}$. Even the extensively optimized basis B does not improve significantly this picture. The respective values are $C_{zz,zz} = 42.53$, $C_{xz,xz} = 35.32$, $C_{xx,xx} = 23.70$ and $\bar{C} = 51.47\, e^2 a_0^4 E_h^{-1}$. Previous calculations by Visser and Wormer [5] and Maroulis and Thakkar [28] are in good agreement with the present values, Dykstra, Liu and Malik [7] used a *spd* basis set and consequently the absence of *f*-GTF results in a $C_{xx,xx}$ component smaller than the other values in Table 1. We mention also the values of $C_{zz,zz} = 42.61$ and $C_{xx,xx} = 23.35\, e^2 a_0^4 E_h^{-1}$ calculated by Diercksen and Sadlej [4] with a $[8s5p3d1f]$ basis set. Both values compare well with ours.

The dipole-octopole polarizability values of Visser and Wormer [5] are $E_{z,zzz} = 52.68$ and $E_{x,xxx} = -35.85\, e^2 a_0^4 E_h^{-1}$. Agreement with our results is better for the parallel component but worsens slightly for the perpendicular one.

$B_{\alpha\beta,\gamma\delta}$ displays strong basis set dependent even for small molecules as hydrogen fluoride [22]. The values obtained with basis A are slightly different from those of basis B. The mean value $\bar{B}$ is -171 and $-169\, e^3 a_0^4 E_h^{-2}$ for A and B, respectively. The only previous values of $B_{\alpha\beta,\gamma\delta}$ are those of Dykstra, Liu and Malik [7]. As expected, the agreement with ours varies, depending on the particular component. It is quite good for $B_{xx,zz}$, but worsens gradually for $B_{xz,xz}$, $B_{zz,zz}$ and $B_{xx,xx}$.

SCF values for $A_{\alpha,\beta\gamma}$, $E_{\alpha,\beta\gamma\delta}$ and $B_{\alpha\beta,\gamma\delta}$ at three bond lengths, 1.932221, 2.132221 and 2.332221 a_0 are given in Table 2. These values have been calculated from the multipole moments induced by homogeneous fields of 0.01 $e^{-1} a_0^{-1} E_h$. The use of rather strong fields accounts, in our opinion, for the small differences between the r_e SCF values in Tables 1 and 2. Strong dependence on the internuclear separation is observed for $E_{\alpha,\beta\gamma\delta}$ and $B_{\alpha\beta,\gamma\delta}$. The values in Table 2 may be used to compute estimates of the first derivative at r_e. For $A_{z,zz}$ and $A_{x,zx}$ we obtain 1.5 and 2.3 $e^2a_0^2E_h^{-1}$, respectively. Amos [2] reported 1.73 and 2.37 $e^2a_0^2E_h^{-1}$.

Electron correlation. Electron correlation affects strongly the parallel component $A_{z,zz}$ and less strongly the perpendicular one $A_{x,zx}$. In absolute terms, the SDQ-MP4 values of $A_{z,zz} = -13.92$ and $A_{x,zx} = -15.01\ e^2a_0^3E_h^{-1}$ are 21.5 and 7.9% larger than the SCF ones. Amos [2] reported configuration interaction (CI) values of $A_{z,zz} = -13.82$ and $A_{x,zx} = -14.46\ e^2a_0^3E_h^{-1}$, in good agreement with ours.

Electron correlation changes the SCF values of $C_{zz,zz}$, $C_{xz,zx}$ and $C_{xx,xx}$ by 9.4, 6.7 and 8.5%, respectively. The correlation corrections for the components of $C_{\alpha\beta,\gamma\delta}$ are somewhat different from those reported by Maroulis and Thakkar [8]. The difference should be attributed to the enlargement of the basis set. The present SDQ-MP4 value of $\bar{C} = 55.12\ e^2a_0^4E_h^{-1}$ is practically identical with the CCD + S(CCD) one of 55.152 $e^2a_0^4E_h^{-1}$. Maroulis and Thakkar [8] found that the T(CCD) correction, the triples contribution calculated with CCD amplitudes, contributes 0.879 $e^2a_0^4E_h^{-1}$ to the mean quadrupole polarizability. This means that the inclusion of $T4$ should be expected to increase the present SDQ-MP4 value of $\bar{C} = 55.12\ e^2a_0^4E_h^{-1}$ by $\approx 1.6\%$. Our $C_{zz,zz}$ and $C_{xx,xx}$ are in good agreement with the SDQ-MP4 values of 46.77 and 25.40 $e^2a_0^4E_h^{-1}$ reported by Diercksen and Sadlej [4].

The SDQ-MP4 values of $E_{z,zzz}$ and $E_{x,xxx}$ are 60.19 and $-38.06\ e^2a_0^4E_h^{-1}$, in absolute terms 11.6 and 4.8% of the respective SCF results. The change of the components of $B_{\alpha\beta,\gamma\delta}$ is strong and uniform. $B_{zz,zz} = -296$, $B_{xz,xz} = -170$, $B_{xx,zz} = 88$ and $B_{xx,xx} = -178\ e^3a_0^4E_h^{-2}$ or 23, 28, 22 and 22% higher in magnitude than the SCF values.

In conclusion, the MP series converges in a satisfactory way for all properties. Electron correlation has a strong effect on the parallel components of the tensors but affects less the perpendicular ones.

5. Conclusions

We have calculated SCF and SDQ-MP4 values of the dipole-quadrupole, quadrupole-quadrupole, dipole-octopole polarizability and the dipole-dipole-quadrupole hyperpolarizability of carbon monoxide.

The SCF values calculated with a very large, carefully optimized [8*s*6*p*5*d*2*f*] basis set are expected to be quite close to the respective Hartree–Fock limit. SDQ-MP4 values were obtained in a smaller, [6*s*4*p*4*d*2*f*] basis set. We are not aware of previous correlated calculations for $E_{\alpha,\beta\gamma\delta}$ and $B_{\alpha\beta,\gamma\delta}$.

We have not attempted to calculate vibrational corrections for the above values. Amos [2] has shown that such effects are rather negligible for the dipole-quadrupole polarizability.

Appendix

Atomic units are used in this work. The conversion factors to SI units are:

Energy, 1 $E_h = 4.3597482 \times 10^{-18}$ J,

Length, 1 $a_0 = 0.529177249 \times 10^{-10}$ m,

$$\mu,\ 1\ ea_0 = 8.478358 \times 10^{-30}\ \mathrm{C\,m},$$

$$\Theta,\ 1\ ea_0^2 = 4.486554 \times 10^{-40}\ \mathrm{C\,m^2},$$

$$\Omega,\ 1\ ea_0^3 = 2.374182 \times 10^{-50}\ \mathrm{C\,m^3},$$

$$\Phi,\ 1\ ea_0^4 = 1.256363 \times 10^{-60}\ \mathrm{C\,m^4},$$

$$A,\ 1\ e^2a_0^3E_h^{-1} = 8.724958 \times 10^{-52}\ \mathrm{C^2\,m^3\,J^{-1}},$$

$$C \text{ or } E,\ 1\ e^2a_0^4E_h^{-1} = 4.617048 \times 10^{-62}\ \mathrm{C^2\,m^4\,J^{-1}},$$

$$B,\ 1\ e^3a_0^4E_h^{-2} = 1.696733 \times 10^{-63}\ \mathrm{C^3\,m^4\,J^{-2}}.$$

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