On the Electric Multipole Moments of Carbon Monoxide

George Maroulis
Department of Chemistry, University of Patras, GR-26110 Patras, Greece

Z. Naturforsch. 47a, 480–484 (1992); received October 11, 1991

The electric dipole, quadrupole, octopole and hexadecapole moment of carbon monoxide has been obtained from finite-field SCF and Moeller-Plesset perturbation theory calculations. The resulting values for the octopole and hexadecapole moments of CO($X^1\Sigma^+$) are $3.59 \, e\cdot a_0^3$ and $-9.01 \, e\cdot a_0^6$, respectively.

Key words: Carbon monoxide, Electric moments, Octopole moment, Hexadecapole moment.

1. Introduction

Electric moments are relevant for many phenomena caused by intermolecular interactions [1–4]. Recent work [5–13] has provided evidence that models relying on the knowledge of the electric moments of the monomers can be used to predict molecular structures and properties of weakly bonded van der Waals systems. Not all electric moments are easily amenable to experiment [2]. Experimental determinations of electric moments beyond the quadrupole are extremely rare. Theory can contribute to the field by predicting these properties.

The electric moments of carbon monoxide have been the object of numerous experimental or theoretical studies [14–27]. Of particular interest to theory is the determination of Hartree-Fock values for the dipole ($\mu$), quadrupole ($\Theta$), octopole ($\Omega$) and hexadecapole ($\Phi$) moments from fully numerical calculations (NHF) by Laaksonen, Pyykkö and Sundholm [22]. This makes possible the construction of Gaussian-type basis sets of near Hartree-Fock quality and the subsequent prediction of accurate electric moments via theoretical methods that take into account electron correlation. In this work we report self-consistent field (SCF) and finite-field Moeller-Plesset perturbation theory (MP) calculations of $\mu$, $\Theta$, $\Omega$, and $\Phi$. The higher moments are extracted from the energies of the molecule perturbed by strategically placed electric point charges. This approach has been followed successfully in previous work on N$_2$ [28], F$_2$ [29], HCl [30] and HCCH [31]. Previous correlated values of $\Omega$ and $\Phi$ for carbon monoxide have been obtained as expectation values of the relevant operators using SD-CI (single and double excitations configuration interaction) wavefunctions. Our approach to the subject has distinct advantages over the SD-CI method [21].

Atomic units are used throughout this work. The conversion factors from atomic to SI units are:

- Energy, $1 \, E_h = 4.3597482 \times 10^{-18} \, J$
- Length, $1 \, a_0 = 0.529177249 \times 10^{-11} \, m$
- Dipole moment, $1 \, e\cdot a_0 = 8.478358 \times 10^{-30} \, Cm$
- Quadrupole moment, $1 \, e\cdot a_0^2 = 4.486554 \times 10^{-40} \, Cm^2$
- Octopole moment, $1 \, e\cdot a_0^3 = 2.374182 \times 10^{-50} \, Cm^3$
- Hexadecapole moment, $1 \, e\cdot a_0^6 = 1.256363 \times 10^{-60} \, Cm^4$.

2. Theory

The energy of an uncharged molecule in a weak electric field can be written as [1, 32]

$$ E = E_0 - \mu_x F_x - (1/3) \Theta_{x\gamma\delta} - (1/15) \Omega_{x\gamma\delta\rho} + (1/105) \Phi_{x\gamma\delta\rho\sigma} + \ldots $$

$$ - (1/2) \lambda_{x\gamma\delta} F_x F_y - (1/3) A_{x\gamma\delta}, F_x F_y + \ldots $$

$$ - (1/6) C_{x\gamma\delta\rho}, F_x F_y F_z - (1/15) E_{x\gamma\delta\rho\sigma}, F_x F_y F_z + \ldots $$

$$ - (1/6) \beta_{x\gamma\delta\rho\sigma}, F_x F_y F_z F_w + \ldots $$

$$ - (1/24) \gamma_{x\gamma\delta\rho\sigma\tau}, F_x F_y F_z F_w F_v + \ldots, $$

where $F_x, F_y, \ldots$ are the field, field gradient, etc. at the origin, $E^0$, $\mu_x$, $\Theta_{x\gamma\delta}$, $\Omega_{x\gamma\delta\rho}$, and $\Phi_{x\gamma\delta\rho\sigma}$ the energy and permanent moments of the free molecule and $\lambda_{x\gamma\delta}$, $\beta_{x\gamma\delta\rho\sigma\tau}$, $A_{x\gamma\delta}$, $C_{x\gamma\delta\rho\sigma\tau}$, $E_{x\gamma\delta\rho\sigma\tau\upsilon}$ and $B_{x\gamma\delta\rho\sigma\tau\upsilon}$ the molec-

0932-0784 / 92 / 0300-0480 $ 01.30 / 0. - Please order a reprint rather than making your own copy.
ular polarizabilities. The greek suffixes denote Cartesian components and a repeated suffix implies summation over \( x, y, \) and \( z \).

For a polar linear molecule like CO there is only one independent component for an electric moment tensor of any order, \( \mu_x, \Theta_{x\beta}, \Omega_{x\beta\gamma}, \Phi_{x\beta\gamma\delta} \) [1]. Therefore we shall simply write \( \mu, \Theta, \Omega \) and \( \Phi \) for the respective properties. The dipole moment is independent of the choice of the origin but the higher moments are not [1].

The electric moments are extracted from (1) by using suitable electric fields. Using a homogeneous electric field, all field-gradient terms are eliminated from (1) and the dipole moment is easily obtained. We give

\[
E_{\text{qd}}(Q, R) \approx E^0 - 6\Theta(Q/R^3)
\]

and

\[
\Theta \approx [E_{\text{qd}}(-Q, R) - E_{\text{qd}}(Q, R)]/(12 Q/R^3).
\]

Placing an array of four charges \(-32 Q, Q, Q, -32 Q\) at \((2R, \pi), (R, \pi), (R, 0), \) and \((R, 0)\) on the molecular axis. Using very distant charges we ensure that higher terms make a negligible contribution to the perturbed energy \( E_{\text{qd}}(Q, R) \), so that

\[
E_{\text{qc}}(Q, R) \approx E^0 + (3/2) \Omega(Q/R^4),
\]

hence

\[
\Omega \approx (2/3) [E_{\text{qc}}(Q, R) - E^0]/(Q/R^4).
\]

Last, a very weak hexadecapolar field is obtained by placing charges of \(-8 Q, Q, Q, -8 Q\) at the same positions as above we simulate a very weak octopolar field, so that

\[
E_{\text{hx}}(Q, R) \approx E^0 + (3/2) \Phi(Q/R^5),
\]

and the hexadecapole moment is calculated as

\[
\Phi \approx (2/3) [E_{\text{hx}}(Q, R) - E^0]/(Q/R^5).
\]

Both SCF and MP values of \( \mu, \Theta, \Omega, \) and \( \Phi \) are calculated from \( E_{\text{qd}}, E_{\text{qc}}, \) and \( E_{\text{hx}} \). Electron correlation corrections are obtained from the fourth-order MP approximation to the perturbed molecular energy. The use of many-body perturbation theory techniques in molecular property calculations has been presented in many comprehensive reviews [33–36].

The fourth-order approximation to the energy is written as

\[
MP4 = \text{SCF} + D2 + D3 + S4 + D4 + T4 + Q4 + R4, \tag{8}
\]

where the fourth order terms are contributions from single, double, triple and quadruple substitutions from the zeroth order wave function and \( R \) the renormalization term. Lower order approximations are defined as

\[
\begin{align*}
\text{MP2} &= \text{SCF} + D2, \\
\text{MP3} &= \text{SCF} + D2 + D3, \\
\text{DQ-MP4} &= \text{MP3} + D4 + Q4 + R4 \\
&= \text{MP3} + DQR4, \\
\text{SDQ-MP4} &= \text{DQ-MP4} + S4. \tag{12}
\end{align*}
\]

By virtue of (8)–(12) we adopt analogous expressions for the molecular properties.

3. Computational Details

All calculations were carried out with a large gaussian-type basis set \((11s^7p^4d^2f)\) contracted to \([6s4p4d2f]\) and consisting of 104 CGTF. The d-GTF and f-GTF are five and seven-membered, respectively. This basis set is the carefully optimized \((11s^7p^3d^2f)\) one used in the calculation of the quadrupole polarizability of CO [26], augmented by one tight d-GTF on carbon and oxygen. The respective exponents are 2.228519 and 2.706063 \(a_0^2\).

A homogeneous field of 0.01 \(e^{-1}a_0^{-1}E_h\) was used in the calculation of the dipole moment. Calculations of \(E(F_z), E(–F_z), E(2F_z)\) and \(E(–2F_z)\) were performed in order to eliminate the contribution of the dipole polarizability and hyperpolarizability and obtain \(\mu_z\). For the calculation of the quadrupole moment from (3) the values of \(Q\) and \(R\) were 200 \(e\) and 100 \(a_0\), respectively. For the octopole moment \(Q = 1000\) \(e\) and \(R = 200\) \(a_0\). A very weak octopolar field is produced from this arrangement, as evidenced by the value of \(Q/R^5 = 6.25 \times 10^{-7} e^{-1}a_0^{-3}E_h\). For the hexadecapole moment \(Q = 10000\) \(e\) and \(R = 200\) \(a_0\), so that \((Q/R^5) = 3.125 \times 10^{-7} e^{-1}a_0^{-4}E_h\).

The SDQ-MP4 approximation to MP4 was adopted in this work. Inclusion of the T4 term would increase dramatically the cost of calculations. The quality of the predictions based on the SDQ-MP4
approximation has been tested in previous work [28, 29, 37]. All calculations were performed with Gaussian 86 [38].

4. Results and Discussion

SCF results: SCF values for $\mu$, $\Theta$, $\Omega$, and $\Phi$ were calculated at three different internuclear separations: the experimental one, $r_e = 2.132221 \ a_0$ [39] and two others, 1.932221 and 2.332221 $a_0$. These values are given in Table 1. Our values at $r_e$ are $-0.1067 \ e a_0$, $-1.52 \ e a_0^2$, $4.42 \ e a_0^3$, and $-10.62 \ e a_0^4$. They compare quite well to the numerical Hartree-Fock values [23] of $-0.104245 \ e a_0$, $-1.53001 \ e a_0^2$, $4.42239 \ e a_0^3$, and $-10.6883 \ e a_0^4$, calculated at 2.132 $a_0$. Agreement is better than 1% for the higher electric moments. Using our values at $r_e=0.2$, $r_e$, and $r_e+0.2$ we obtained, via a parabolic fit, estimates of the first derivatives of the electric moments at $r_e$: $(d\mu/dr) = -1.0165 \ e$, $(d\Theta/dr) = 22.55 \ e a_0^2$, and $(d\Omega/dr) = -8.10 \ e a_0^2$ for $\mu$, $\Theta$, $\Omega$, and $\Phi$, respectively.

Correlated results: Electron correlation corrections to the electric moments of CO were calculated at the SDQ-MP4 level and are given in Table 2. The behaviour of the MP series for $\mu$ and $\Theta$ displays quite different patterns from those present in the case of $\Omega$ or $\Phi$. The D2 correction for $\mu$ is quite large, more important in size than the SCF value and of opposite sign. Consequently, MP2, MP3, DQ-MP4, and SDQ-MP4 are positive. Electron correlation changes only slightly the SCF $\Theta$ result. Convergence is rather slow for this property, as D2, D3, and S4 + D4 + QR4 are roughly of the same size at 0.03, 0.05, and $-0.04 \ e a_0^2$. Convergence is quite good for either $\Omega$ or $\Phi$. Electron correlation reduces the magnitude of both properties. The SDQ-MP4 values are $3.59 \ e a_0^3$ and $-9.01 \ e a_0^4$, 19 and 15% lower (in absolute terms) than the respective SCF ones.

Comparison to other predictions and experiment. Theoretical predictions and experimental data for the electric moments of CO are presented in Table 3. It is easily seen that the SCF values are close enough to the respective NHF limits for all fairly large basis sets. Electron correlation changes the sign of the dipole moment. Correlated methods invariably predict the correct sign but fail to produce a close agreement with the experimental value of $0.04881 \ e a_0$ [16]. A SD-CI calculation by Amos [19] gave 0.1370 $e a_0$. The MBPT(4) (complete fourth-order many-body perturbation theory) result of Diercksen and Sadlej [21] is still far from the experimental one at 0.1024 $e a_0$. The same authors have also reported a SD-CI value of 0.0435 $e a_0$, calculated with the same basis set as the above, quite close to the experimental one. Feller, Boyle, and Davidson [24] reported SD-CI and MRSD-CI (multireference SD-CI) values of 0.0205 and 0.0400 $e a_0$, respectively. An approximate coupled-cluster doubles (ACCD) calculation by Dykstra, Liu, and Malik [25] gave 0.0357 $e a_0$. The most accurate theoretical prediction is presumably the 0.0492 $e a_0$ reported by Scuseria et al. [27] who used a large [10s9p4d2f1g] basis set and the CCSD(T) (coupled-cluster single, double and connected triple excitations). Our SDQ-MP4 value of 0.0580 $e a_0$ is 0.01 $e a_0$ above the experimental value. We predict a total correlation correction of 0.1647 $e a_0$, to be compared with the 0.1536 $e a_0$ of Scuseria et al. [27].

The theoretical methods fare better in the prediction of the quadrupole moment. Theory predicts the value of $\Theta$ in the region of $-1.45$ to $-1.52 \ e a_0^2$. The present calculation gave $-1.48 \ e a_0^2$. This is quite close to a value of $-1.502 \ e a_0^2$ obtained by Maroulis...
Table 3. Comparison of theoretical and experimental values of the electric multipole moments of CO ($X^1\Sigma^+$).

<table>
<thead>
<tr>
<th>Method</th>
<th>$\mu$</th>
<th>$\Theta$</th>
<th>$\Omega$</th>
<th>$\Phi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SCF $^a$</td>
<td>-0.1016</td>
<td>-1.5016</td>
<td>4.4070</td>
<td>-10.5742</td>
</tr>
<tr>
<td>SCF $^b$</td>
<td>-0.1040</td>
<td>-1.5078</td>
<td>4.4453</td>
<td>-10.3074</td>
</tr>
<tr>
<td>SCF $^c$</td>
<td>-0.0993</td>
<td>-1.5238</td>
<td>4.433</td>
<td>-10.785</td>
</tr>
<tr>
<td>SCF $^d$</td>
<td>-0.106</td>
<td>-1.540</td>
<td>4.435</td>
<td>-10.73</td>
</tr>
<tr>
<td>SCF $^e$</td>
<td>-0.1045</td>
<td>-1.5355</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SCF $^f$</td>
<td>-0.0911</td>
<td>-1.5486</td>
<td>4.4205</td>
<td></td>
</tr>
<tr>
<td>SCF $^g$</td>
<td>-0.112</td>
<td>-1.537</td>
<td>4.403</td>
<td>-10.552</td>
</tr>
<tr>
<td>SCF $^h$</td>
<td>-0.1044</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SCF $^i$</td>
<td>-0.105</td>
<td>-1.547</td>
<td>4.354</td>
<td>-10.403</td>
</tr>
<tr>
<td>SCF $^j$</td>
<td>-0.101</td>
<td>-1.508</td>
<td>4.438</td>
<td>-10.689</td>
</tr>
<tr>
<td>SCF $^k$</td>
<td>-0.102</td>
<td>-1.513</td>
<td>4.422</td>
<td>-10.631</td>
</tr>
<tr>
<td>SCF $^l$</td>
<td>-0.107</td>
<td>-1.537</td>
<td>4.394</td>
<td>-10.695</td>
</tr>
<tr>
<td>SCF $^m$</td>
<td>-0.1067</td>
<td>-1.52</td>
<td>4.42</td>
<td>-10.62</td>
</tr>
<tr>
<td>ELP $^n$</td>
<td>-0.104245</td>
<td>-1.53001</td>
<td>4.42239</td>
<td>-10.6883</td>
</tr>
<tr>
<td>SD-CI $^o$</td>
<td>0.1370</td>
<td>-1.4499</td>
<td>3.7710</td>
<td>-9.4185</td>
</tr>
<tr>
<td>MBPT(4) $^p$</td>
<td>0.1024</td>
<td>-1.5195</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SD-CI $^q$</td>
<td>0.0435</td>
<td>-1.5164</td>
<td>3.903</td>
<td>-9.848</td>
</tr>
<tr>
<td>MRSD-CI $^r$</td>
<td>0.0400</td>
<td>-1.5219</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ACCD $^s$</td>
<td>0.0357</td>
<td>-1.4902</td>
<td>3.8196</td>
<td></td>
</tr>
<tr>
<td>CCD + ST(CCD) $^t$</td>
<td>-1.502</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CCSD(T) $^u$</td>
<td>0.0492</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SDQ-MP4 $^v$</td>
<td>0.0580</td>
<td>-1.48</td>
<td>3.59</td>
<td>-9.01</td>
</tr>
<tr>
<td>Experiment</td>
<td>0.0481</td>
<td>$-1.5 \pm 0.7$</td>
<td>$-1.4 \pm 0.1$</td>
<td>$-1.44 \pm 0.3$</td>
</tr>
</tbody>
</table>

$^a$ Basis set [5s4p2d] at 2.132 $a_0$ [19].
$^b$ Basis set [24s12p4d] at 2.13263 $a_0$ [20].
$^c$ Basis set [8s5p3d1f] at 2.132 $a_0$ [21].
$^d$ Basis set [6s5p3d2f] [22].
$^e$ Basis set [10s6p4d2f] at 2.132 $a_0$ [24].
$^f$ ELP basis set at 2.132221 $a_0$ [25].
$^g$ Basis set [8s4p3d2f] at 2.132221 $a_0$ [26].
$^h$ Basis set [10s9p4d2f1g] at 2.1316 $a_0$ [27].
$^i$ Basis sets [6s4p3d1f], [6s4p4d1f], [6s4p4p1f] and [6s4p3d2f] at 2.132221 $a_0$. Unpublished results by Maroulis and Thakkar.
$^j$ SDQ-MP4.
$^k$ Experimental.
$^l$ Fully numerical values at a bond length of 2.132 $a_0$ [23].
$^m$ Stark effect measurements [16].
$^n$ Microwave asymmetric Zeeman shifts [14].
$^o$ Far IR rotational spectra [15].
$^p$ Molecular beam electric resonance Stark-Zeeman spectra [17].
$^q$ Ion molecule scattering cross sections [18].

5. Conclusions

We have reported SDQ-MP4 values for the electric dipole, quadrupole, octopole and hexadecapole moments of ground state carbon monoxide. Our values for $\Omega$ and $\Phi$ should be the most accurate currently available. Our estimates for these properties are $\Omega = 3.6 \pm 0.2 e \alpha_0^3$ and $\Phi = -9.0 \pm 0.5 e \alpha_0^4$.

Acknowledgements

The author is happy to acknowledge the generous hospitality of the Computer Centre of the Computer Technology Institute (ITY) of Patras.