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Accurate electric multipole moments for HCN and HCP from CCSD(T) calculations with large gaussian basis sets

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Summary. Accurate values of the electric multipole moments of HCN and HCP have been obtained from self-consistent field (SCF) and coupled-cluster (CCSD(T)) calculations. With the origin at the centre of mass and hydrogen along the positive molecular axis in both systems, a [9*s*5*p*2*d*/10*s*7*p*5*d*3*f*/10*s*7*p*5*d*3*f*] basis set is expected to predict near-Hartree–Fock values for the dipole ($\mu = 1.2962ea_0$), quadrupole ($\Theta = 2.1046ea_0^2$), octopole ($\Omega = 10.088ea_0^3$) and the hexadecapole ($\Phi = 24.23ea_0^4$) moment of HCN. An analogous basis set, [9*s*5*p*2*d*/10*s*7*p*5*d*3*f*/14*s*11*p*7*d*3*f*], predicts SCF values of $\mu = 0.1421ea_0$, $\Theta = 3.8786ea_0^2$, $\Omega = 19.633ea_0^3$ and $\Phi = 65.89ea_0^4$ for HCP. Electron correlation reduces the dipole moment of HCN but increases the dipole moment of HCP. At the CCSD(T) level of theory the calculated values are $\mu = 1.1800ea_0$, $\Theta = 1.6461ea_0^2$, $\Omega = 9.762ea_0^3$ and $\Phi = 22.45ea_0^4$ for HCN and $\mu = 0.1710ea_0$, $\Theta = 3.2312ea_0^2$, $\Omega = 16.578ea_0^3$ and $\Phi = 60.87ea_0^4$ for HCP.

Key words: HCN–HCP – Dipole moment – quadrupole moment – Octopole moment – Hexadecapole moment

1 Introduction

The theory of electric multipole moments occupies a central position in the description and interpretation of intermolecular interactions and related phenomena [1–3]. The use of these properties in theoretical models used in predictions of molecular geometries [4] and properties [5] of weakly bonded van der Waals molecules justifies the need for accurate values. Experimental techniques provide reliable values of the dipole (μ) and quadrupole (Θ) moment [2, 6] but the accurate determination of the higher multipoles is quite difficult. Remarkably, few measurements of the octopole (Ω) and hexadecapole (Φ) moment have been reported.

The electric moments of HCN and HCP have been the object of several theoretical [7–17] and experimental [18–23] studies. The theoretical determinations

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are usually limited to self-consistent field (SCF) studies. Accurate methods have been applied to the study of electron correlation effects for the dipole and the quadrupole moment but in most cases rely on small or medium sized basis sets. No experimental values are known for the octopole and hexadecapole moment of either molecule. In this paper we present a systematic study of μ, Θ, Ω and Φ for HCN and HCP. We report finite-field many-body perturbation theory and coupled cluster calculations with large Gaussian basis sets. The properties are extracted from the energy of the molecule perturbed by weak multipolar fields produced by arrays of strategically placed distant point charges, a method applied with success in the case of HCCH [24], HCl [25], CO [26], Cl_2 [27] and H_2CCH_2 [28].

Atomic units are used throughout this work. Conversion factors to SI units are given in the appendix.

2 Theory

The energy of an uncharged molecule in a sufficiently weak, general electric field can be written as [29, 30]

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

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

For linear molecules there is only one independent component for any multipole moment tensor [6]. We drop the subscripts and write μ, Θ, Ω, Φ for the dipole, quadrupole, octopole and hexadecapole moment, respectively. The extraction of the electric moments from Eq. (1) has been presented in some detail elsewhere [24–28]. We use a very weak homogeneous electric field to calculate the dipole moment from

$$E(F_z) \cong E^0 - \mu F_z. \qquad (2)$$

We use strategically placed arrays of distant point charges to simulate very weak quadrupolar, octopolar and hexadecapolar fields and obtain the respective electric moments from equations similar to (2). This approach is followed for the calculation of both SCF and correlated values.

Full fourth-order many-body perturbation theory (MP4) and coupled-cluster methods were used for the evaluation of electron correlation effects. We refer to an excellent review paper by Urban et al. [31] for a presentation of MP. The various MP approximations, up to the fourth order, to the molecular energy are written as (see [32] for details)

$$
\begin{aligned}
\mathrm{MP2} &= \mathrm{SCF} + \mathrm{D2},\\
\mathrm{MP3} &= \mathrm{MP2} + \mathrm{D}_3,\\
\text{DQ-MP4} &= \mathrm{MP3} + \mathrm{D4} + \mathrm{Q4} + \mathrm{R4},\\
\text{SDQ-MP4} &= \text{DQ-MP4} + \mathrm{S4},\\
\mathrm{MP4} &= \text{SDQ-MP4} + \mathrm{T4}.
\end{aligned}
\tag{3}
$$

The coupled-cluster (CC) techniques used in this work are CCSD, single and double excitation coupled-cluster theory, and its extension CCSD(T) which includes an estimate of connected triple excitations (T) via a perturbational treatment [33]. In analogy to Eq. (3) we write

$$\mathrm{CCSD(T)} = \mathrm{SCF} + \Delta\mathrm{CCSD} + \mathrm{T}. \tag{4}$$

It is both essential and instructive to compare the calculated MP values to those obtained by the much more (computationally) expensive CC techniques. Recent work has revealed the existence of characteristic patterns in comparisons of MP and CC calculations of electric properties [33].

3 Basis sets and computational details

The CCSD(T) calculations for HCN were carried out with a basis set consisting of $(6s3p2d/11s7p4d3f/11s7p4d3f)$ primitive set of Gaussian-type functions (GTF) contracted to $[4s3p2d/6s4p4d3f/6s4p4d3f]$, 141 contracted GTF. For HCP we used a $[6s3p2d/11s7p4d2f/13s9p5d3f]$ basis set contracted to $[4s3p2d/6s4p4d2f/8s6p5d3f]$, 147 CGTF. Both sets were built upon substrates of $(4s)$ $[2s]$ for H [35], $(9s5p)$ $[4s2p]$ for C, N [35] and $(11s7p)$ $[6s4p]$ for P [36]. These substrates were augmented with diffuse and polarization functions. The resulting basis sets are given in Table 1.

Smaller versions of the aforedescribed sets were used to study basis set effects on the calculated properties. These are $[4s2p1d/6s4p4d1f/6s4p4d1f]$ (hereafter NA) and $[4s3p2d/6s4p4d2f/6s4p4d2f]$ (NB) for HCN while the respective HCP basis sets are $[4s2p1d/6s4p4d1f/8s6p4d1f]$ (hereafter PA) and $[4s3p2d/6s4p4d2f/8s6p4d2f]$ (PB). The large basis sets used in the CCSD(T) calculations are NC and PC for HCN and HCP, respectively.

In a final effort we used two very large sets to obtain electric moments of near-Hartree–Fock quality. These were built upon an uncontracted $(7s)$ substrate for H [38], a $(13s8p)$ $[8s5p]$ one for C, N [37] and $(17s12p)$ $[12s9p]$ for P [38]. The final sets, expected to give properties of near-Hartree–Fock quality, consist of 188 CGTF for HCN, $[9s5p2d/10s7p5d3f/10s7p5d3f]$ (basis ND) and 214 CGTF for HCP, $[9s5p2d/10s7p5d3f/14s11p5d3f]$ (basis PD).

Further details of the construction and the optimization of the polarization functions are given elsewhere [39].

Very weak fields were used in the calculations. A homogeneous field of $0.000001 E_h e^{-1} a_0^{-1}$ was used in the calculation of the dipole moment. For the quadrupole, octopole and hexadecapole moment the charges used produce very weak quadrupolar, octopolar and hexadecapolar fields, as $|Q/R^3| = 0.000001 E_h e^{-1} a_0^{-2}$, $|Q/R^4| = 0.000000625 E_h e^{-1} a_0^{-3}$ and $|Q/R^5| = 0.0000003125 E_h e^{-1} a_0^{-4}$, respectively.

Table 1. Description of basis sets used in the CCSD(T) calculations. Gaussian function exponents are given in a_0^{-2}

Description	HCN	HCP
Substrate		
Primitive	(4*s*/9*s*5*p*/9*s*5*p*)	(4*s*/9*s*5*p*/11*s*7*p*)
Contracted	[2*s*/4*s*2*p*/4*s*2*p*]	[2*s*/4*s*2*p*/6*s*4*p*]
Additional functions		
Diffuse	H *s*: 0.048273, 0.013121	H *s*: 0.048273, 0.013121
	C *s*: 0.047362, 0.014632	C *s*: 0.047362, 0.014632
	p: 0.036542, 0.011652	*p*: 0.036542, 0.011652
	N *s*: 0.064996, 0.019805	P *s*: 0.044959, 0.016327
	p: 0.051481, 0.016024	*p*: 0.036976, 0.010982
Polarization	H *p*: 0.8882, 0.1795, 0.036276	H *p*: 1.0280, 0.1585, 0.024438
	d: 0.1795, 0.036276	*d*: 0.1585, 0.024438
	C *d*: 1.731353, 0.7036 0.1162, 0.019191	C *d*: 1.004789, 0.4390, 0.0838, 0.015996
	f: 0.7036, 0.1162, 0.019191	*f*: 0.4390, 0.0838
	N *d*: 2.128064, 0.8085 0.1167, 0.016845	P *d*: 1.274266, 0.5178, 0.210409, 0.0855, 0.014118
	f: 0.8085, 0.1167, 0.016845	*f*: 0.5178, 0.0855, 0.014118
Final basis set	[4*s*3*p*2*d*/6*s*4*p*4*d*3*f*/6*s*4*p*4*d*3*f*]	[4*s*3*p*2*d*/6*s*4*p*4*d*2*f*/8*s*6*p*5*d*3*f*]
Number of CGTF	141	147

For HCN the two innermost orbitals were kept frozen in the correlated calculations, while excitations to the two highest virtual orbitals were not allowed. Thus, ten electrons were correlated. In the case of HCP the six innermost orbitals were kept frozen and excitations to the six highest virtual orbitals were not allowed.

All calculations were performed at the experimental molecular geometry. For HCN, $R_{CH} = 1.06549$ Å and $R_{CN} = 1.15321$ Å [40]. For HCP, $R_{CH} = 1.0692$ Å and $R_{CP} = 1.5398$ Å [41]. The higher multipole moments are relative to the centre of mass. Hydrogen lies along the positive part of the molecular axis.

Gaussian 92 was used in the calculations [42].

4 Results and discussion

SCF. SCF results are shown in Table 2. Stable values are obtained for the electric moments of HCN. Agreement is better than 1% for the dipole and nearly of the same order for the octopole moment. Agreement is also quite good for the quadrupole and the hexadecapole moment. The difficulty of obtaining reliable values for the higher multipole moments is well known [43, 44].

The dipole moment of HCP is considerably smaller than that of HCN. The PC value of $0.1379ea_0$ is 3% lower than the presumably more accurate PD of $0.1421ea_0$, but in absolute terms the difference is only $0.0042ea_0$. It is worth noticing that the agreement between the two basis sets is remarkably good for the higher multipoles, better than 1% in all cases.

Table 2. Convergence of SCF values. The dipole moment is origin independent. The higher moments are relative to the centre of mass. Hydrogen lies along the positive part of the molecular axis

Basis set	μ/ea_0	μ/ea_0	Θ/ea_0^2	Ω/ea_0^3	Φ/ea_0^4
HCN					
NA	$[4s2p1d/6s4p4d1f/6s4p4d1f]$[a]	1.2987	2.0981	10.120	23.26
NB	$[4s3p2d/6s4p4d2f/6s4p4d2f]$[b]	1.2983	2.0563	10.126	23.13
NC	$[4s3p2d/6s4p4d3f/6s4p4d3f]$[c]	1.2982	2.0591	10.137	23.59
ND	$[9s5p2d/10s7p5d3f/10s7p5d3f]$[d]	1.2962	2.1046	10.088	24.23
HCP					
PA	$[4s2p1d/6s4p4d1f/8s6p4d1f]$[e]	0.1483	3.8912	19.652	65.75
PB	$[4s3p2d/6s4p4d2f/8s6p4d2f]$[f]	0.1450	3.8268	19.648	64.20
PC	$[4s3p2d/6s4p4d2f/8s6p5d3f]$[g]	0.1379	3.8424	19.675	65.82
PD	$[9s5p2d/10s7p5d3f/14s11p5d3f]$[h]	0.1421	3.8786	19.633	65.89

[a] $6d/10f$ (six-membered d-GTF and ten-membered f-GTF), 120 contracted GTF

[b] $5d/7f$, 127 CGTF

[c] $5d/7f$, 141 CGTF

[d] $5d/7f$, 188 CGTF. SCF energy $-92.91310162E_h$

[e] $6d/10f$, 128 CGTF

[f] $5d/7f$, 135 CGTF

[g] $5d/7f$, 147 CGTF

[h] $5d/7f$, 214 CGTF. SCF energy $-379.15712736E_h$

Electron correlation effects. Electron correlation corrections are given in Table 3 for HCN and Table 4 for HCP.

Electron correlation has a uniform effect on the electric moments of HCN. The final CCSD(T) values are $\mu = 1.1800ea_0$, $\Theta = 1.6461ea_0^2$, $\Omega = 9.762ea_0^3$ and $\Phi = 22.45ea_0^4$, representing a reduction by 9.1%, 20.1%, 3.7% and 4.8% of the respective SCF values. Thus, the dipole and quadrupole moment values are strongly affected by electron correlation, while the effect is less important in the case of the higher multipoles. Convergence is fast for the MP series. Consequently the MP4 results compare very well with the CCSD(T) ones and a similar agreement is observed between the SDQ-MP4 and CCSD values.

The MP series converges slowly for the dipole moment of HCP. The D2 and D3 corrections are nearly equal. The T4 correction is relatively large for this property. The MP2, MP3 and MP4 values display an important fluctuation. The CCSD and CCSD(T) values are 0.1483 and $0.1710ea_0$, 7.5% and 24.0%, respectively, above the SCF value of $0.1379ea_0$. The CCSD(T) values of $\Theta = 3.2312ea_0^2$, $\Omega = 16.578ea_0^3$ and $\Phi = 60.87ea_0^4$, are 15.9%, 15.7% and 7.5% lower than the SCF values of $\Theta = 3.8424ea_0^2$, $\Omega = 19.675ea_0^3$ and $\Phi = 65.82ea_0^4$. With the notable exception of the dipole moment, the pattern observed for HCN is visible for HCP as well. The MP4 and SDQ-MP4 values are remarkably close to the CCSD(T) and CCSD ones, respectively.

Comparison with previous theoretical efforts and experiment. A selection of previous theoretical endeavours is displayed in Table 5 (HCN) and 6 (HCP). We list only efforts that go beyond the calculation of the dipole moment.

Gready et al. [7] reported SCF values of μ, Θ, Ω and Φ calculated with a small basis set. A systematic study of basis set effects of μ, Θ and Ω at the SCF level was

Table 3. Electron correlation corrections[a] to the electric multipole moments of HCN. Basis set NC [4*s*3*p*2*d*/6*s*4*p*4*d*3*f*/6*s*4*p*4*d*3*f*]. The quadrupole, octopole and hexadecapole moments are relative to the centre of mass. Hydrogen lies along the positive part of the molecular axis

Method	μ/ea_0	Θ/ea_0^2	Ω/ea_0^3	Φ/ea_0^4
SCF	1.2982	2.0591	10.137	23.59
D2	−0.1070	−0.4582	−0.197	−0.49
D3	0.0099	0.1527	−0.012	−0.18
S4	−0.0021	−0.0252	−0.079	−0.10
D4	−0.0149	−0.0670	−0.044	−0.16
T4	−0.0190	−0.0545	−0.049	0.11
QR4	0.0148	0.0163	−0.015	−0.15
ΔCCSD	−0.1018	−0.3784	−0.034	−1.17
T	−0.0164	−0.0346	−0.040	0.03
MP2	1.1912	1.6009	9.940	23.11
MP3	1.2011	1.7536	9.929	22.93
DQ-MP4	1.2010	1.7029	9.869	22.62
SDQ-MP4	1.1989	1.6777	9.790	22.52
MP4	1.1799	1.6232	9.741	22.63
CCSD	1.1964	1.6807	9.802	22.42
CCSD(T)	1.1800	1.6461	9.762	22.45

[a] With reference to the zeroth-order SCF value, D2 and D3 are the second and third-order corrections to the property. The fourth-order corrections S4, D4, T4 correspond to single, double, triple substitutions with respect to the SCF wave function while QR4 sum up quadruple substitutions and the renormalization term. ΔCCSD is the total correction resulting from the single and double excitation coupled cluster treatment and T is the estimate of the connected triple excitations contribution. See also text, Sect. 2

Table 4. Electron correlation corrections[a] to the electric multipole moments of HCP. Basis set PC [4*s*3*p*2*d*/6*s*4*p*4*d*2*f*/8*s*6*p*5*d*3*f*]. The quadrupole, octopole and hexadecapole moments are relative to the centre of mass. Hydrogen lies along the positive part of the molecular axis

Method	μ/ea_0	Θ/ea_0^2	Ω/ea_0^3	Φ/ea_0^4
SCF	0.1379	3.8424	19.675	65.82
D2	0.0528	−0.6460	−3.351	−4.48
D3	−0.0530	0.1800	0.943	1.34
S4	0.0166	−0.0262	−0.116	−0.31
D4	0.0157	−0.0775	−0.527	−0.97
T4	0.0450	−0.0805	−0.616	−0.17
QR4	−0.0150	0.0343	0.317	−0.46
ΔCCSD	0.0104	−0.5487	−2.715	−4.89
T	0.0228	−0.0625	−0.382	−0.06
MP2	0.1907	3.1964	16.324	61.34
MP3	0.1377	3.3764	17.267	62.68
DQ-MP4	0.1384	3.3332	17.056	61.25
SDQ-MP4	0.1550	3.3070	16.941	60.95
MP4	0.2000	3.2265	16.324	60.78
CCSD	0.1483	3.2937	16.960	60.93
CCSD(T)	0.1710	3.2312	16.578	60.87

[a] See footnote to Table 3

Table 5. Comparison of theoretical and experimental results for the electric multipole moments of HCN

Method	μ/ea_0	Θ/ea_0^2	Ω/ea_0^3	Φ/ea_0^4
Theory				
SCF[a]	1.308	1.508	8.944	17.051
SCF[b]	1.290	2.051	10.420	
SCF[b]	1.296	2.098	9.985	
SCF[c]	1.2075	1.8918		
MP4[c]	1.1648	1.6235		
SCF[d]	1.2692	2.2585		
SD-CI[d]	1.1831	1.9531		
SCF[e]	1.2997	2.0876	10.0468	
ACCD[e]	1.1954	1.7486	9.8266	
SCF[f]	1.275	1.688		
QCISD[f]	1.149	1.272		
SCF[g]	1.2962	2.1046	10.088	24.22
SCF[h]	1.2982	2.0591	10.137	23.59
CCSD[h]	1.1964	1.6807	9.802	22.42
CCSD(T)[h]	1.1800	1.6461	9.762	22.45
Experiment	1.174 ± 0.002[i]	2.6 ± 0.7[l]		
	1.18[j]	2.3 ± 0.4[m]		
	1.187 ± 0.001[k]			

[a] Calculated with a $[5s4p1d/3s1p]$ basis set at a molecular geometry defined by bond lengths of $R_{CH} = 2.009a_0$ and $R_{CN} = 2.153a_0$ [7]

[b] At the experimental geometry, basis sets DZPP and LPP [8]

[c] Basis set 6–311 G(*d*/*p*) [9]

[d] Basis set 6–311 G(2*d*/2*p*) [9]

[e] ELP basis set, $R_{CH} = 1.1531$ Å and $R_{CN} = 1.0659$ Å [10]

[f] Basis set 6–31 G(*d*, *p*) [12]

[g] Present investigation, basis set$[9s5p2d/10s7p5d3f/10s7p5d3f]$ (188 CGTF)

[h] Present investigation, basis set $[4s3p2d/6s4p4d3f/6s4p4d3f]$ (141 CGTF)

[i] Bhattacharya and Gordy [18]

[j] Tyler and Sheridan [19]

[k] DeLeon and Muenter [23]

[l] Gustafson and Gordy [21]

[m] Hartfort et al. [22]

carried out by Van Duijneveldt-Van de Rijdt and Van Duijneveldt [8]. Their large LPP set gives values in good agreement with ours. Sokalski and Sawaryn [9] used standard basis set to calculate SCF and correlated values for the dipole and quadrupole moment. The trends observed in their MP4 and SD-CI (configuration interaction with single and double excitations) results agree well with ours. Dykstra et al. [10] reported SCF and ACCD (approximate coupled cluster theory with double substitutions) values of the dipole, quadrupole and octopole moment. Their SCF values are in good agreement with ours. Their ACCD result for the octopole moment of HCN is, to our knowledge, the only correlated value for Ω reported in the literature. This value of $9.8266ea_0^3$ was obtained with a basis set smaller than ours but agrees quite well with our CCSD result of $9.802ea_0^3$. Kraka et al. [12] obtained SCF and QCISD (quadratic SD-CI) results for the dipole and quadrupole moment in a small standard basis set. They obtained QCISD values of $\mu = 1.149ea_0$ and $\Theta = 1.272ea_0^2$, with the latter value rather lower than our

Table 6. Comparison of theoretical and experimental results for the electric multipole moments of HCP

Method	μ/ea_0	Θ/ea_0^2	Ω/ea_0^3	Φ/ea_0^4
Theory				
SCF[a]	0.287	3.27		
QCISD[a]	0.244	2.67		
SCF[b]	0.1421	3.8786	19.633	65.89
SCF[c]	0.1379	3.8424	19.675	65.82
CCSD[c]	0.1483	3.2937	16.960	60.93
CCSD(T)[c]	0.1710	3.2312	16.578	60.87
Experiment	0.153 ± 0.002[d]	3.3 ± 0.9[e]		

[a] Basis set 6–31 G(*d*, *p*) [12]
[b] Present investigation, basis set [9*s*5*p*2*d*/10*s*7*p*5*d*3*f*/14*s*11*p*5*d*3*f*] (214 CGTF)
[c] Present investigation, basis set [4*s*3*p*2*d*/6*s*4*p*4*d*2*f*/8*s*6*p*5*d*3*f*] (147 CGTF)
[d] Tyler [20]
[e] Hartford et al. [22]

correlated quadrupole moments in Table 5. Last, we mention the CCSD(T) dipole moment of $1.148ea_0$ obtained with a DZ + P basis set by Thomas et al. [14] and another value of $1.176ea_0$ obtained with a TZ(2*df*,2*pd*) basis set by Thomas et al. [15]. The latter, calculated with a large basis set, is close to our CCSD(T) result.

The old experimental values of the dipole moment of HCN, by Bhattacharya and Gordy [18] and Tyler and Sheridan [19] are in good agreement with the more recent value of $\mu_e = 1.187 \pm 0.001ea_0$ reported by DeLeon and Muenter [23]. This value is in excellent agreement with our CCSD(T) result of $1.1800ea_0$. The experimental estimates of the quadrupole moment reported by Gustafson and Gordy [21] and Hartford et al. [22] are characterized by large uncertainties and are systematically higher than our best correlated values.

Both the SCF and QCISD dipole moment for HCP reported by Kraka et al. [12] are considerably higher than our respective values. The opposite is observed in the case of the quadrupole moment where their values are lower than ours. This may safely be attributed to the fact that basis set effects are more important for HCP. A recent study by Goldstein et al. [16] showed that no correlation treatment will produce stable values for the dipole moment of HCP if the basis set is not suitably large. These authors reported MP2 and CASSCF (complete active space SCF) values calculated with various basis sets. A MP2/6–311 G** value of $0.181ea_0$ may be compared to a CASSCF one of $0.248ea_0$ calculated with a TZV + + ** basis set. We mention also the MRSDCI (multireference SDCI) dipole moment of $0.181ea_0$ by Karna et al. [11] and the DFT (density functional theory) values of $0.153ea_0$ (local density approximation, LDA) and $0.142ea_0$ (nonLDA) reported by Chong [13]. The experimental value of the dipole moment is $0.153 \pm 0.002ea_0$ [20], between CCSD and CCSD(T) results. Our values agree quite well with the experimental value of the quadrupole moment, $\Theta = 3.3 \pm 0.9ea_0^2$ reported by Hartford et al. [22].

5 Conclusions

We have calculated accurate values for the dipole, quadrupole, octopole and hexadecapole moment of HCN and HCP using coupled cluster theory, CCSD(T) and large basis sets of Gaussian-type functions. Our final values for HCN are $\mu = 1.1800ea_0$, $\Theta = 1.6461ea_0^2$, $\Omega = 9.762ea_0^3$ and $\Phi = 22.45ea_0^4$. For HCP we obtained $\mu = 0.1710ea_0$, $\Theta = 3.2312ea_0^2$, $\Omega = 16.578ea_0^3$ and $\Phi = 60.87ea_0^4$.

Agreement is excellent with the equilibrium experimental dipole moment of HCN reported by DeLeon and Muenter [23]. It should be mentioned that the experimental values pertain to the ground vibrational state while our values are calculated at the experimental equilibrium geometry. Thus, in a strict sense, our values for the remaining properties are not directly comparable to the experimental ones. Nevertheless, it is instructive to note the kind of agreement observed in such cases as it may point to situations worth of further investigation. For HCN theory predicts quadrupole moments systematically lower than experiment. For HCP agreement with experiment is good for both the dipole and the quadrupole moment. For both systems the experimental quadrupole moments are characterized by large uncertainties. We are not aware of any experimental estimates for the octopole and hexadecapole moment.

Appendix

The following conversion factors from atomic to SI units are adopted in this work:

Energy, $1E_h = 4.3597482 \times 10^{-18}$ J,
Length, $1a_0 = 0.529177249 \times 10^{-10}$ m,
μ, $1ea_0 = 8.478358 \times 10^{-30}$ Cm,
Θ, $1ea_0^2 = 4.486554 \times 10^{-40}$ Cm^2,
Ω, $1ea_0^3 = 2.374182 \times 10^{-50}$ Cm^3,
Φ, $1ea_0^4 = 1.256363 \times 10^{-60}$ Cm^4.

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