

Molecules in static electric fields: Linear and nonlinear polarizability of HC≡N and HC≡P

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Accurate linear and nonlinear polarizabilities were obtained from finite-field self-consistent field, fourth-order many-body perturbation theory and coupled-cluster calculations for the triply bonded linear molecules H—C≡N and H—C≡P. The mean dipole polarizability and the anisotropy of HCN at the CCSD(T) level of theory is $\bar{\alpha} = 16.74$ and $\Delta\alpha = 8.38e^2a_0^2E_H^{-1}$. For HCP the respective values are 35.47 and $16.24e^2a_0^2E_H^{-1}$. Electron correlation reduces significantly the magnitude of the first dipole hyperpolarizability ($\beta_{\alpha\beta\gamma}$) of both molecules. The CCSD(T) values of the mean $\bar{\beta}$ are [self-consistent-field (SCF) values in parentheses] -2.8 (-7.6) for HCN and 28.5 (36.7) $e^3a_0^3E_H^{-2}$ for HCP. Electron correlation modifies mainly the longitudinal component of the second hyperpolarizability tensor $\gamma_{\alpha\beta\gamma\delta}$ for both HCN and HCP. The CCSD(T) mean value for HCN is $\bar{\gamma} = 22.0 \times 10^2$, 17.4% higher than the SCF value of $18.8 \times 10^2 e^4 a_0^4 E_H^{-3}$. For HCP $\bar{\gamma} = 10.2 \times 10^3$ at the CCSD(T) level, only 2.2% above the SCF result of $99.8 \times 10^2 e^4 a_0^4 E_H^{-3}$. For the quadrupole polarizability, fourth-order many-body perturbation theory yields $C_{zz,zz} = 68.58$, $C_{xz,xz} = 40.51$, $C_{xx,xx} = 34.98 e^2 a_0^4 E_H^{-1}$ for HCN, and $C_{zz,zz} = 202.28$, $C_{xz,xz} = 114.44$, $C_{xx,xx} = 106.38 e^2 a_0^4 E_H^{-1}$ for HCP, with z as the molecular axis. [S1050-2947(98)01804-6]

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I. INTRODUCTION

Experimental information on the electric properties of HCN and HCP is limited mostly to measurements of the dipole and quadrupole moment [1–6]. Spackman [7] references a static value for the mean dipole polarizability of HCN obtained from the refractive index dispersion data of Watson and Ramaswamy [8]. The available theoretical determinations of the electric polarizability of HCN and HCP are mainly self-consistent-field (SCF) efforts [9–12]. To our knowledge, electron correlation effects have only been taken into account for the dipole polarizability of HCN [13–15].

In a previous paper [16] we reported accurate values for the dipole (μ), quadrupole (Θ), octopole (Ω), and hexadecapole (Φ) moment of both molecules. In this paper we present a detailed study of the linear and nonlinear polarizability, molecular properties of importance for nonlinear optics [17,18], electron scattering [19], and the interpretation of various phenomena induced by intermolecular interactions [20]. They also find use in models predicting the structure and properties of weakly bonded van der Waals molecules [21,22]. It is worth noticing that in recent years the theoretical determination of electric molecular hyperpolarizabilities has made significant contributions to the above-mentioned fields by providing reliable values to be used in specific applications [23–27]. Lucid expositions of the success of quantum chemical methods and the directions of current research have appeared in various comprehensive reviews [28–32].

We are interested in determining very accurate values for

the dipole polarizability ($\alpha_{\alpha\beta}$). The nonlinear polarizability ($\beta_{\alpha\beta\gamma}$ and $\gamma_{\alpha\beta\gamma\delta}$) of HCN is known only at the SCF level of theory while for HCP only the first dipole hyperpolarizability is known. The SCF study of this property by Bloor and Yu [11] showed that its values are strongly basis-set dependent. It would be interesting to obtain accurate estimates of the electron correlation effects on the nonlinear polarizability of these systems, the smallest neutral molecules with a triple C≡N or C≡P bond. Our computational endeavors rely on fourth-order Møller-Plesset perturbation theory (MP4), single and double excitation (CCSD), and single, double, and perturbative triple excitation [CCSD(T)] coupled-cluster methods.

We use atomic units throughout this paper except when referring to experimental molecular geometries where we retain the units of the original papers. Conversion factors to Système International units have been given elsewhere [33].

II. THEORY

The energy of an uncharged molecule perturbed by a weak, general electric field can be written as [34,35]

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

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where F_α , $F_{\alpha\beta}$, etc. 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 the dipole, quadrupole, octopole, and hexadecapole moment of the free molecule. The second-, third-, and fourth-order properties are the dipole polarizability ($\alpha_{\alpha\beta}$), the first ($\beta_{\alpha\beta\gamma}$) and second ($\gamma_{\alpha\beta\gamma\delta}$) dipole hyperpolarizability, the dipole-quadrupole polarizability ($A_{\alpha,\beta\gamma}$), the quadrupole polarizability ($C_{\alpha\beta,\gamma\delta}$), the dipole-octopole polarizability ($E_{\alpha,\beta\gamma\delta}$), and the dipole-dipole-quadrupole hyperpolarizability ($B_{\alpha\beta,\gamma\delta}$). The subscripts denote Cartesian components and a repeated subscript implies summation over x , y , and z . There is only one independent component for the electric multipole moment tensors of linear molecule, so hereafter we drop the subscript and write μ , Θ , Ω , and Φ . The number of independent components needed to describe the polarizability tensors depends on the molecular symmetry [34].

The SCF and correlated values of the dipole properties μ , $\alpha_{\alpha\beta}$, $\beta_{\alpha\beta\gamma}$, and $\gamma_{\alpha\beta\gamma\delta}$ were extracted from the energy of the molecule perturbed by a homogeneous electric field. In such a field Eq. (1) reduces to

$$E = E^0 - \mu_\alpha F_\alpha - \frac{1}{2} \alpha_{\alpha\beta} F_\alpha F_\beta - \frac{1}{6} \beta_{\alpha\beta\gamma} F_\alpha F_\beta F_\gamma - \frac{1}{24} \gamma_{\alpha\beta\gamma\delta} F_\alpha F_\beta F_\gamma F_\delta + \dots \quad (2)$$

The relevant formulas for the calculation of the independent components can be found elsewhere [33]. For the calculation of the quadrupole polarizability $C_{\alpha\beta,\gamma\delta}$ we use arrays of strategically placed, distant point charges that produce a weak, quadrupolar electric field [36,37]. We have also obtained SCF values for the remaining polarizabilities from the induced multipole moments [38,39].

In addition to the Cartesian components, we calculate mean values and anisotropies for the dipole polarizabilities $\alpha_{\alpha\beta}$, $\beta_{\alpha\beta\gamma}$, and $\gamma_{\alpha\beta\gamma\delta}$ and mean values for $C_{\alpha\beta,\gamma\delta}$ and $B_{\alpha\beta,\gamma\delta}$. These are defined as

$$\begin{aligned} \bar{\alpha} &= (\alpha_{zz} + 2\alpha_{xx})/3, \\ \Delta\alpha &= \alpha_{zz} - \alpha_{xx}, \\ \bar{\beta} &= \frac{3}{5}(\beta_{zzz} + 2\beta_{zxx}), \\ \bar{\gamma} &= (3\gamma_{zzzz} + 8\gamma_{xxxx} + 12\gamma_{xxzz})/15, \\ \bar{C} &= (C_{zz,zz} + 8C_{xz,xz} + 8C_{xx,xx})/10, \\ \bar{B} &= \frac{2}{15}(B_{zz,zz} + 4B_{xz,xz} + B_{xx,zz} + 4B_{xx,xx}). \end{aligned} \quad (3)$$

We refer to other authors for a presentation of electron correlation methods used in this paper [40–46]. We give only the definitions for the various levels of theory. The energy for the n th-order Møller-Plesset perturbation theory, MPn, is defined as

$$\text{MP2} = \text{SCF} + \text{D2}$$

$$\text{MP3} = \text{MP2} + \text{D3}$$

$$\text{DQ} - \text{MP4} = \text{MP3} + \text{D4} + \text{QR4} = \text{MP3} + \text{DQ4} \quad (4)$$

$$\text{SDQ} - \text{MP4} = \text{DQ} - \text{MP4} + \text{S4}$$

$$\text{MP4} = \text{SDQ} - \text{MP4} + \text{T4} \equiv \text{SCF} + \text{D2} + \text{D3} + \text{S4}$$

$$+ \text{D4} + \text{T4} + \text{Q4} + \text{R4},$$

where D2 and D3 are the second- and third-order corrections, the fourth-order terms S4, D4, T4, and Q4 are contributions from single, double, triple, and quadruple substitutions from the reference, zeroth-order wave function, and R4 is the renormalization term. For the coupled-cluster methods

$$\text{CCSD} = \text{SCF} + \Delta\text{CCSD}, \quad (5)$$

$$\text{CCSD}(T) = \text{CCSD} + T.$$

By virtue of Eq. (1) we adopt for all properties expansions similar to those of Eqs. (4) and (5).

III. BASIS SET CONSTRUCTION

A. HCN

Three basis sets were used for the calculations on HCN:

(i) N1, primitive set ($6s2p1d/11s7p4d1f/11s7p4d1f$) contracted to [$4s2p1d/6s4p4d1f/6s4p4d1f$] with six-membered d -GTF and ten-membered f -GTF, $6d/10f$, in total 120 contracted Gaussian-type functions (GTF).

(ii) N2, ($6s3p2d/11s7p4d2f/11s7p4d2f$)/[$4s3p2d/6s4p4d2f/6s4p4d2f$], $5d/7f$, 127 CGTF.

(iii) N3, ($9s5p2d/15s10p5d3f/15s10p5d3f$)/[$9s5p2d/10s7p5d3f/10s7p5d3f$], $5d/7f$, 188 CGTF. N1 and N2 were built upon a DZ substrate [47] of ($4s$)[$2s$] on H and ($9s5p$)[$4s2p$] on either C or N. The initial DZ substrate was augmented to [$4s/6s4p/6s4p$] by adding diffuse GTF with exponents forming a geometric progression with the two most diffuse ones in the original set. In a next step, polarization functions were added on all atoms. First, one tight p -GTF on H and one tight d -GTF on C and N with exponents chosen to minimize the energy of the free molecule. Second, one diffuse p -GTF on H and one diffuse d -GTF on C and N with exponents chosen to maximize the mean dipole polarizability. To complete the construction of N1, two d -GTF were added on C and N, plus one d -GTF on H and one f -GTF on C and N. The exponents of the latter are equal to the most diffuse (polarizability optimized) p - or d -GTF. More polarization functions were added, even-temperedly, to complete the construction of N1. Thus, the polarization functions for N1 are the following: for H, $p=0.8882$, 0.1795 and $d=0.1795$; for C, $d=1.731353$, 0.7063 , 0.1162 , 0.019191 and $f=0.1162$; for N, $d=2.128064$, 0.8085 , 0.1167 , 0.016845 and $f=0.1167$. N2 is obtained from N1 by adding: on H, $p=0.036276$, $d=0.036276$; on C, $f=0.7036$; on N, $f=0.8085$.

The construction of N3 follows the same path. The substrate is an uncontracted set ($7s$) [48] for H and ($13s8p$)[$8s5p$] [49] for either C or N. We give directly the polarization functions that complete the construction of N3:

H: $p=2.381\ 99$, $1.030\ 25$, 0.4456 , $0.192\ 73$, $0.036\ 05$ and $d=0.192\ 73$, $0.036\ 05$.

C: $d=2.0900$, $0.841\ 05$, $0.338\ 45$, 0.1362 , $0.022\ 06$ and $f=0.338\ 45$, 0.1362 , $0.022\ 06$.

N: $d=1.781\ 56$, $0.750\ 25$, $0.319\ 54$, $0.133\ 05$, $0.023\ 60$ and $f=0.319\ 54$, $0.133\ 05$, $0.023\ 60$.

B. HCP

The basis set used for the calculations on HCP are

P1, $(6s2p1d/11s7p4d1f/13s9p4d1f)[4s2p1d/6s4p4d1f/8s6p4d1f]$, $6d/10f$, 128 CGTF.

P2, $(6s3p1d/11s7p4d2f/13s9p4d2f)[4s3p2d/6s4p4d2f/8s6p4d2f]$, $5d/7f$, 135 CGTF.

P3, $(9s5p2d/15s10p5d3f/19s14p7d3f)[9s5p2d/10s7p5d3f/14s11p7d3f]$, $5d/7f$, 214 CGTF.

The substrates used are as above for H and C and for P ($11s7p$)[$6s4p$] [50] for P1 and P2 and ($17s12p$)[$12s9p$] [48] for P3. The polarization functions on P1 are as follows:

H: $p=1.0280$, 0.1585 and $d=0.1585$;

C: $d=1.004\ 789$, 0.4390 , 0.0838 , $0.015\ 996$ and $f=0.0838$;

P: $d=1.274\ 266$, 0.5178 , 0.0855 , $0.014\ 118$ and $f=0.0855$.

In addition to P1, P2 has $p=0.0244\ 38$, $d=0.0244\ 38$ on H, $f=0.4390$ on C, and $f=0.5178$ on P.

Last, the polarization functions on P3 are as follows:

H: $p=2.532\ 41$, $0.997\ 92$, $0.393\ 24$, $0.154\ 96$, $0.024\ 06$ and $d=0.154\ 96$, $0.024\ 06$,

C: $d=1.644\ 67$, $0.605\ 18$, $0.222\ 68$, $0.081\ 94$, 0.01109 and $f=0.222\ 68$, $0.081\ 94$, $0.011\ 09$,

P: $d=3.036\ 18$, $1.234\ 75$, $0.502\ 15$, $0.204\ 21$, $0.083\ 05$, $0.013\ 74$, $0.002\ 27$ and

$f=0.204\ 21$, 0.08305 , 0.01374 .

In our previous work on the electric moments of HCN and HCP we used even larger versions of basis sets N2 and P2. Details of their construction may be found therein [16].

IV. COMPUTATIONAL DETAILS

The magnitude of the homogeneous electric field used in the correlated calculations of the dipole polarizability and hyperpolarizability is $F=0.005e^{-1}a_0^{-1}E_H$. In the SCF calculations with N3 and P3 an even weaker field of $0.003e^{-1}a_0^{-1}E_H$ was used. We used strategically placed distant point charges to generate a weak quadrupolar field for the quadrupole polarizability calculations. For HCN, placing charges of $-3200, 100, 100, -3200\ e$ at $-200, -100, 100, 200\ a_0$ on the z axis produces a weak field with $|q/R^3|=0.0001e^{-1}a_0^{-2}E_H$. For HCP the same charges are placed at $-400, -200, 200, \text{ and } 400\ a_0$, producing an even weaker field of $0.000\ 0125\ e^{-1}a_0^{-2}E_H$.

All calculations pertain to the experimental geometry, defined as $R_{CH}=1.06549\ \text{\AA}$ and $R_{CN}=1.15321\ \text{\AA}$ for HCN

[51] and $R_{CH}=1.0692\ \text{\AA}$ and $R_{CP}=1.5398\ \text{\AA}$ for HCP [52]. The molecule is always on the z axis with the center of mass at the origin and the H along the positive part of the axis. The GAUSSIAN 86 and GAUSSIAN 92 set of programs [53] was used in all calculations.

V. RESULTS AND DISCUSSION

SCF results are shown in Table I. Electron correlation corrections for HCN (basis N2) and HCP (basis P2) are given in Tables II and III, respectively. The linear and non-linear dipole polarizabilities are compared to the findings of other authors in Table IV.

A. SCF

The electric multipole moments in Table I have already been published elsewhere [16]. They are included here to allow a complete comparison of the performance of the basis sets used in this work.

TABLE I. SCF results (z is the molecular axis, with H on the positive direction and the center of mass at the origin). Θ , Ω , Φ , $A_{\alpha\beta\gamma}$, $C_{\alpha\beta\gamma\delta}$, $E_{\alpha\beta\gamma\delta}$ and $B_{\alpha\beta\gamma\delta}$, are relative to the center of mass. Numbers in brackets are powers of ten, i.e., 16.2[2] is 16.2×10^2 . All values are in atomic units.

Property ^a	HCN ^b	HCN ^c	HCN ^d	HCP ^e	HCP ^f	HCP ^g
μ	1.2987	1.2983	1.2962	0.1483	0.1450	0.1421
Θ	2.0981	2.0563	2.1046	3.8912	3.8268	3.8786
Ω	10.120	10.126	10.088	19.652	19.648	19.633
Φ	23.26	23.13	24.23	65.75	64.20	65.89
α_{zz}	22.46	22.46	22.47	47.97	48.08	48.02
α_{xx}	13.79	13.79	13.88	30.97	30.95	31.12
$\bar{\alpha}$	16.68	16.68	16.74	36.64	36.66	36.75
$\Delta\alpha$	8.67	8.67	8.59	17.00	17.13	16.90
β_{zzz}	-6.9	-6.6	-6.3	45.0	45.6	45.8
β_{zxx}	-2.8	-3.0	-3.0	8.8	7.8	9.1
$\bar{\beta}$	-7.5	-7.6	-7.4	37.6	36.7	38.4
γ_{zzzz}	16.2[2]	16.2[2]	16.2[2]	73.2[2]	74.2[2]	72.4[2]
γ_{xxxx}	19.6[2]	19.9[2]	20.3[2]	10.8[3]	11.0[3]	11.3[3]
γ_{xxzz}	60.0[1]	61.4[1]	62.4[1]	32.7[2]	32.8[2]	33.5[2]
$\bar{\gamma}$	18.5[2]	18.8[2]	19.1[2]	98.7[2]	99.8[2]	10.2[3]
$A_{z,zz}$	11.05	11.11	10.93	54.74	54.71	54.46
$A_{x,zx}$	1.98	2.02	1.93	7.28	7.57	7.03
$C_{zz,zz}$	63.53	63.51	63.43	202.22	202.77	202.42
$C_{xz,xz}$	36.71	36.93	37.10	115.79	115.42	116.97
$C_{xx,xx}$	33.82	34.15	34.21	113.49	113.90	115.25
\bar{C}	62.78	63.21	63.39	203.65	203.73	206.02
$E_{z,zzz}$	85.14	84.37	83.95	231.7	238.4	231.8
$E_{x,xxx}$	-26.97	-26.95	-27.35	-69.0	-67.2	-70.2
$B_{zz,zz}$	-326	-326	-323	-1083	-1117	-1090
$B_{xz,xz}$	-206	-210	-210	-867	-870	-880
$B_{xx,zz}$	166	169	167	745	751	746
$B_{xx,xx}$	-266	-271	-266	-1155	-1178	-1175
\bar{B}	-273	-277	-275	-1124	-1141	-1142

^aThe values of μ , Θ , Ω , Φ are from Maroulis and Pouchan [16].

^bBasis set N1 [4s2p1d/6s4p4d1f/6s4p4d1f], 6d/10f, 120 CGTF.

^cN2 [4s3p2d/6s4p4d2f/6s4p4d2f], 5d/7f, 127 CGTF.

^dN3 [9s5p2d/10s7p5d3f/10s7p5d3f], 5d/7f, 188 CGTF.

^eP1 [4s2p1d/6s4p4d1f/8s6p4d1f], 6d/10f, 128 CGTF.

^fP2 [4s3p2d/6s4p4d2f/8s6p4d2f], 5d/7f, 135 CGTF.

^gP3 [9s5p2d/10s7p5d3f/14s11p7d3f], 5d/7f, 214 CGTF.

The stability of the obtained values is very satisfactory, for both systems. For the dipole polarizability agreement is better than 1% in all cases. The large basis sets, N3 and P3, yield a slightly less anisotropic picture of $\alpha_{\alpha\beta}$. For the first and second dipole hyperpolarizability, the values obtained with basis sets N1,N2 and P1,P2 are within a few percent of the presumably more accurate N3,P3 results. The first dipole hyperpolarizability changes sign from HCN to HCP [54]. Agreement is equally satisfactory for the other polarizabilities. Thus, we can claim uniform quality for the basis sets N2 and P2, which are subsequently used in electron correlation correction calculations.

Previous theoretical efforts have produced SCF values for various HCN properties included in this effort. In their inter-

esting study, Jameson and Fowler [9] used a [5s4p2d1f/3s2p] basis set to obtain $\alpha_{zz}=22.389$ and $\alpha_{xx}=13.736 e^2 a_0^2 E_H^{-1}$, $\beta_{zzz}=6.386$ and $\beta_{zxx}=-3.434 e^3 a_0^3 E_H^{-2}$, $\gamma_{zzzz}=1533$, $\gamma_{xxxx}=1840$ and $\gamma_{xxzz}=564 e^4 a_0^4 E_H^{-3}$ for the dipole polarizability and hyperpolarizability. They also obtained $A_{z,zz}=10.96$ and $A_{x,zx}=1.90 e^2 a_0^3 E_H^{-1}$, $B_{zz,zz}=-319$, $B_{xz,xz}=-204$, $B_{xx,zz}=162$, and $B_{xx,xx}=-263 e^3 a_0^4 E_H^{-2}$. Our values are in very good agreement with the aforementioned, although our hyperpolarizability values are systematically slightly different from theirs. This may be safely attributed to the fact that our basis sets contain more diffuse and polarization functions. Dykstra's work, derivative Hartree-Fock (DHF) theory, has pro-

TABLE II. Electron correlation corrections to the dipole and quadrupole properties of HCN. (The two innermost, occupied orbitals and the two highest, virtual orbitals were kept frozen in all calculations.) Basis set N2 $[4s3p2d/6s4p4d2f/6s4p4d2f]$. Numbers in brackets are powers of ten, i.e., 16.2[2] is 16.2×10^2 . All values are in atomic units.

Property	SCF	MP2	MP3	DQ-MP4	SDQ-MP4	MP4	CCSD	CCSD(T)
μ	1.2983	1.1912	1.2010	1.2009	1.1989	1.1801	1.1966	1.1805
Θ	2.0560	1.5990	1.7511	1.7005	1.6751	1.6208		
α_{zz}	22.46	21.87	22.00	21.91	22.09	22.42	22.07	22.32
α_{xx}	13.79	13.92	13.81	13.70	13.72	13.96	13.77	13.95
$\bar{\alpha}$	16.68	16.57	16.54	16.44	16.51	16.78	16.53	16.74
$\Delta\alpha$	8.67	7.95	8.20	8.22	8.37	8.46	8.30	8.38
β_{zzz}	-6.6	0.2	-1.4	-0.4	-4.0	-7.6	-3.1	-5.4
β_{zxx}	-3.0	1.1	-0.7	0.3	0.3	0.0	0.5	0.4
$\bar{\beta}$	-7.6	1.4	-1.7	0.1	-2.0	-4.5	-1.3	-2.8
γ_{zzzz}	16.2[2]	23.9[2]	20.4[2]	20.8[2]	22.0[2]	24.2[2]	23.1[2]	25.0[2]
γ_{xxxx}	19.9[2]	20.9[2]	19.9[2]	18.9[2]	19.0[2]	21.2[2]	19.7[2]	21.1[2]
γ_{xxzz}	61.4[1]	72.1[1]	65.9[1]	63.8[1]	65.3[1]	73.3[1]	67.0[1]	72.2[1]
$\bar{\gamma}$	18.8[2]	21.7[2]	20.0[2]	19.3[2]	19.7[2]	22.0[2]	20.5[2]	22.0[2]
$C_{zz,zz}$	63.51	68.68	66.07	66.68	67.14	68.58		
$C_{xz,xz}$	36.93	40.73	38.86	39.09	39.43	40.51		
$C_{xx,xx}$	34.15	34.81	34.16	34.09	34.27	34.98		
\bar{C}	63.21	67.30	65.02	65.21	65.68	67.25		

TABLE III. Electron correlation corrections to the dipole and quadrupole properties of HCP. (The six innermost, occupied orbitals and the six highest, virtual orbitals were kept frozen in all calculations.) Basis set P2 $[4s3p2d/6s4p4d2f/8s6p4d2f]$. Numbers in brackets are powers of ten, i.e., 74.2[2] is 74.2×10^2 . All values are in atomic units.

Property	SCF	MP2	MP3	DQ-MP4	SDQ-MP4	MP4	CCSD	CCSD(T)
μ	0.1450	0.1792	0.1252	0.1288	0.1469	0.1868	0.1390	0.1577
Θ	3.8268	3.1656	3.3493	3.3056	3.2853	3.2089		
α_{zz}	48.08	45.93	46.14	46.00	46.33	46.78	46.06	46.30
α_{xx}	30.95	30.29	30.11	29.86	29.85	30.16	29.87	30.05
$\bar{\alpha}$	36.66	35.50	35.45	35.24	35.34	35.70	35.27	35.47
$\Delta\alpha$	17.13	15.64	16.03	16.14	16.49	16.62	16.19	16.24
β_{zzz}	45.6	6.0	23.7	22.1	29.5	28.9	22.7	21.8
β_{zxx}	7.8	11.0	10.3	10.6	12.6	15.4	11.2	12.9
$\bar{\beta}$	36.7	16.8	26.5	26.0	32.8	35.8	27.1	28.5
γ_{zzzz}	74.2[2]	94.3[2]	91.7[2]	88.7[2]	88.4[2]	95.1[2]	86.4[2]	91.4[2]
γ_{xxxx}	11.0[3]	11.0[3]	11.1[3]	10.5[3]	10.5[3]	11.4[3]	10.2[3]	10.6[3]
γ_{xxzz}	32.8[2]	35.8[2]	37.0[2]	34.9[2]	34.9[2]	38.2[2]	32.0[2]	33.8[2]
$\bar{\gamma}$	99.8[2]	10.6[3]	10.7[3]	10.2[3]	10.2[3]	11.0[3]	97.3[2]	10.2[3]
$C_{zz,zz}$	202.77	202.01	198.51	198.35	199.38	202.28		
$C_{xz,xz}$	115.42	115.36	113.30	112.41	112.68	114.44		
$C_{xx,xx}$	113.90	104.77	105.66	104.99	106.08	106.38		
\bar{C}	203.73	196.31	195.02	193.75	194.94	196.88		

TABLE IV. Comparison of theoretical and experimental results for the electric properties of HCN and HCP.

Method	μ	$\bar{\alpha}$	$\Delta\alpha$	$\bar{\beta}$	$\bar{\gamma}$
HCN					
SCF ^a	1.2966	16.620	8.653	-7.952	1740
SCF ^b	1.328	16.333	9.455		
MP2 ^b	1.163	16.109	8.407		
SCF ^c	1.291	16.656	8.852		
CCSDT-1A ^c	1.171	16.745	8.850		
SCF ^d	1.2950	16.754	8.610	-6.85	181.6
SCF ^e	1.2962	16.7404	8.5892	-7.4	19.1×10 ²
SCF ^f	1.2983	16.6800	8.6733	-7.6	18.8×10 ²
CCSD(T) ^f	1.1805	16.7388	8.3776	-2.8	22.0×10 ²
Experiment	1.174±0.002 ^g 1.18 ^h 1.187±0.001 ⁱ	16.74 ^j			
HCP					
SCF ^k		36.70	16.92	38.66	
SCF ^l	0.1421	36.75	16.90	38.4	10.2×10 ³
SCF ^m	0.1450	36.66	17.13	36.7	99.8×10 ²
CCSD(T) ^m	0.1577	35.47	16.24	28.5	10.2×10 ³
Experiment	0.153±0.002 ⁿ				

^aJameson and Fowler, basis set [3s2p/5s4p2d1f/5s4p2d1f] [9].

^bSpackman, basis set 6-31G(+sd+sp) [7].

^cFowler and Diercksen, basis set [3s2p/5s3p2d/5s3p2d] [14].

^dStählerin *et al.* [3+1s2+1p1+1d]+2s1p1d on H, [4+1s3+1p2+1d1+1f]+2s2p1d1f on C and N [12].

^ePresent investigation, basis set N3, [9s5p2d/10s7p5d3f/10s7p5d3f].

^fPresent investigation, basis set N2, [4s3p2d/6s4p4d2f/6s4p4d2f].

^gBhattacharya and Gordy [1].

^hTyler and Sheridan [2].

ⁱDeLeon and Muentzer [6].

^jReferenced by Spackman [7].

^kBloor and Yu, basis set TZ, 6D, 4P2D 122 CGTF [11].

^lPresent investigation, basis set P3, [9s5p2d/10s7p5d3f/14s11p7d3f].

^mPresent investigation, basis set P2, [4s3p2d/6s4p4d2f/8s6p4d2f].

ⁿTyler [3].

vided valuable information about the dipole and quadrupole polarizability for an important collection of molecular systems [10,55]. As he uses unabridged tensors, we have converted his values to conform to Buckingham's conventions. Thus, his ELP basis set gives $\alpha_{zz}=22.40$ and $\alpha_{xx}=13.75 e^2 a_0^2 E_H^{-1}$, $A_{z,zz}=11.06$ and $A_{x,zx}=1.70 e^2 a_0^3 E_H^{-1}$, $C_{zz,zz}=62.92$, $C_{xz,xz}=35.94$ and $C_{xx,xx}=26.80 e^2 a_0^4 E_H^{-1}$, $B_{zz,zz}=-317$, $B_{xz,xz}=-203$, $B_{xx,zz}=160$ and $B_{xx,xx}=-221 e^3 a_0^4 E_H^{-2}$. The absence of *d*-GTF on H and *f*-GTF on C and N in the ELP basis set should account for the difference between his and our values for either $C_{xx,xx}$ or $B_{xx,xx}$. Last, we mention the results obtained by Stählerin *et al.* [12] with a basis set consisting of [3+1s2+1p1+1d]+(2s1p1d) on H and [4+1s3+1p2+1d1+1f]+(2s2p1d1f) on C and N, $\alpha_{zz}=22.494$ and $\alpha_{xx}=13.884 e^2 a_0^2 E_H^{-1}$, $\beta_{zzz}=5.63$ and

$\beta_{zxx}=-2.89 e^3 a_0^3 E_H^{-2}$, $\gamma_{zzzz}=1641$, $\gamma_{xxxx}=2061$ and $\gamma_{xxzz}=629 e^4 a_0^4 E_H^{-3}$. Our $\beta_{\alpha\beta\gamma}$ values are somewhat different from theirs, but it should be mentioned that their results pertain to a slightly different molecular geometry. If this difference is taken into consideration, agreement between our results and theirs is quite good. We mention also that our values are in very good agreement with the SCF values $\alpha_{zz}=22.52$ and $\alpha_{xx}=13.79 e^2 a_0^2 E_H^{-1}$ reported recently by Grayson and Raynes [56].

In sharp contrast to HCN, HCP has attracted much less attention. The careful study of Bloor and Yu [11] showed that the SCF values of $\alpha_{\alpha\beta}$ and $\beta_{\alpha\beta\gamma}$ calculated with standard basis sets display strong basis set dependence. The largest basis set used in their study, built upon a D95++ substrate and consisting of 132 CGTF, gives $\alpha_{zz}=47.95$ and

$\alpha_{xx} = 31.14 e^2 a_0^2 E_H^{-1}$, $\beta_{zzz} = 45.46$ and $\beta_{zzx} = 10.69 e^3 a_0^3 E_H^{-2}$. Given the small difference in the molecular geometry, our values are in good agreement with theirs.

B. Electron correlation corrections

Accurate μ and Θ values for HCN and HCP, calculated with basis sets larger than N2 and P2, have been reported previously [16]. We include the correlated values in Tables II and III for the sake of completeness.

HCN. The CCSD(T) value of $\mu = 1.1805 e a_0$ is very close to our previous one of $1.1800 e a_0$. Equally close is the agreement of the Θ values. The MP4 value of $1.6208 e a_0^2$ compares quite well with the $1.6232 e a_0^2$ reported elsewhere [16].

Electron correlation has a small effect on the dipole polarizability. Our final CCSD(T) values for the Cartesian components of $\alpha_{\alpha\beta}$ are very close to the respective SCF values. The longitudinal component decreases slightly while the transversal one increases. Consequently, the CCSD(T) value of $16.74 e^2 a_0^2 E_H^{-1}$ is only 0.4% higher than the SCF value. The CCSD(T) anisotropy is $8.38 e^2 a_0^2 E_H^{-1}$ or 3.3% lower than the SCF result. The MP series displays satisfactory convergence, as evidenced by the closeness of the SDQ-MP4 values to the CCSD ones and the MP4 to CCSD(T). The hyperpolarizability is clearly more affected, with the MP series converging slowly. The extreme behavior is exemplified by the MP2 results, which differ drastically from the other levels of theory. The CCSD(T) mean $\bar{\beta}$ is significantly smaller in magnitude than the SCF one. The changes are less drastic in the case of $\gamma_{\alpha\beta\gamma\delta}$. The MP series converges in a satisfactory way. The CCSD(T) results show that electron correlation does not affect isotropically the components of the second dipole hyperpolarizability. The CCSD(T) values are $\gamma_{zzzz} = 25.0 \times 10^2$, $\gamma_{zzxz} = 72.2 \times 10^1$, and $\gamma_{xxxx} = 21.1 \times 10^2 e^4 a_0^4 E_H^{-3}$; that is, 54.3, 17.6, and 6.0% higher than the respective SCF values. Consequently, electron correlation changes the mean $\bar{\gamma}$ by 17.0%. For $C_{\alpha\beta,\gamma\delta}$ the changes are similar. The most affected component is $C_{zz,zz}$. The other components change slightly. The final MP4 value for \bar{C} is 67.25, 6.4% higher than the SCF result of $63.21 e^2 a_0^4 E_H^{-1}$.

Previous correlated calculations for the dipole polarizability or hyperpolarizability are limited to $\alpha_{\alpha\beta}$. Spackman [7] obtained MP2 values of $\bar{\alpha} = 16.109$ and $\Delta\alpha = 8.407 e^2 a_0^2 E_H^{-1}$ with a 6-31G(+*sd*+*sp*) basis set. Fowler and Diercksen [14] reported coupled cluster values of $\bar{\alpha} = 16.745$ and $\Delta\alpha = 8.850 e^2 a_0^2 E_H^{-1}$ calculated with a [3*s*2*p*/5*s*3*p*2*d*/5*s*3*p*2*d*] basis. We mention also two partial efforts, a PE-MCSF (pair-excited multiconfigurational SCF) [13] of $\bar{\alpha} = 15.80 e^2 a_0^2 E_H^{-1}$ calculated with a TZ+2P basis set and the CASSCF (complete active space multiconfigurational SCF) [15] $\Delta\alpha = 8.14 e^2 a_0^2 E_H^{-1}$ obtained with a [5*s*3*p*1*d*/8*s*7*p*3*d*1*f*/8*s*7*p*3*d*1*f*] basis. Our values are in fair agreement with all of the above.

HCP The present CCSD(T) value of the dipole moment is $0.1577 e a_0$, lower than that previously published [16]. The difference is rather small in absolute terms but shows that even if the dipole moment is small in magnitude electron correlation effects are strongly basis set dependent. Similar behavior has been detected in CO, another system with a small dipole moment [33]. The MP4 value of the quadrupole moment agrees quite well with the earlier result. Electron

correlation has a small effect on both components of $\alpha_{\alpha\beta}$. In contrast to the changes observed for HCN, both Cartesian components decrease in magnitude. Thus the mean dipole polarizability at the CCSD(T) level is 3.2% lower than the SCF values. The change for the anisotropy is slightly more important, as the CCSD(T) value of 16.24 is 5.2% lower than the SCF one of $17.13 e^2 a_0^2 E_H^{-1}$. The first and second dipole hyperpolarizability display the same pattern as in the case of HCN. The longitudinal components are the most affected. The sign of the correction for γ_{zzzz} and γ_{xxxx} is negative. Thus, in total, the change for $\bar{\gamma}$ is small as the CCSD(T) value is 10.2×10^3 , only 2.2% higher than the SCF result of $99.8 \times 10^2 e^4 a_0^4 E_H^{-3}$. $C_{zz,zz}$ and $C_{xz,xz}$ are less affected than $C_{xx,xx}$ by the introduction of electron correlation effects. The MP4 value of $C_{xx,xx}$ is $106.38 e^2 a_0^4 E_H^{-1}$, 6.6% lower than the SCF one of $113.90 e^2 a_0^4 E_H^{-1}$. This results in a MP4 value of $\bar{C} = 196.88 e^2 a_0^4 E_H^{-1}$, a reduction of 3.4% of the 203.73 $e^2 a_0^4 E_H^{-1}$ obtained at the SCF level. We are not aware of any previous correlated values for this molecule.

C. Comparison with experiment

The values of μ and Θ for HCN and HCP reported here are in good agreement with the available experimental data, with the notable exception of the quadrupole moment of HCN. This has been discussed elsewhere [16] (see Table IV).

The only reliable experimental polarizability value is the static mean dipole polarizability of HCN [8,57], $16.74 e^2 a_0^2 E_H^{-1}$. This value pertains to the ground vibrational state. We have not taken into account vibrational effects in this study. Our CCSD(T) result of $16.74 e^2 a_0^2 E_H^{-1}$ should be a reliable value for this property at the experimental equilibrium geometry.

VI. CONCLUSIONS

We have obtained a reference, near Hartree-Fock values for the polarizabilities of the triply bonded linear molecules HCN and HCP. We have calculated CCSD(T) values for linear and nonlinear polarizability. In addition we have calculated MP4 values for the quadrupole polarizability of both systems. To our knowledge, with the exception of the dipole polarizability of HCN, these are the first correlated values of these properties to appear in the literature. The calculated, vibrationless, mean dipole polarizability of HCN is $16.74 e^2 a_0^2 E_H^{-1}$, close to the experimental value of $16.74 e^2 a_0^2 E_H^{-1}$ obtained from refractive index dispersion data. The CCSD(T) mean dipole polarizability and the anisotropy reported here for HCP, $\bar{\alpha} = 35.47$ and $\Delta\alpha = 16.24 e^2 a_0^2 E_H^{-1}$, should be the only accurate dipole polarizability data available for this molecule. Electron correlation has a very strong effect on the first dipole hyperpolarizability. It affects mainly the longitudinal component of $\gamma_{\alpha\beta\gamma\delta}$.

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- [1] B. N. Bhattacharya and W. Gordy, *Phys. Rev.* **119**, 144 (1960).
- [2] J. K. Tyler and J. Sheridan, *Trans. Faraday Soc.* **59**, 2661 (1963).
- [3] J. K. Tyler, *J. Chem. Phys.* **40**, 1170 (1964).
- [4] S. Gustafson and W. Gordy, *J. Chem. Phys.* **58**, 5181 (1973).
- [5] S. L. Hartford, W. C. Allen, C. L. Norris, E. F. Pearson, and W. H. Flygare, *Chem. Phys. Lett.* **18**, 153 (1973).
- [6] R. L. DeLeon and J. S. Muentner, *J. Chem. Phys.* **80**, 3992 (1984).
- [7] M. A. Spackman, *J. Phys. Chem.* **93**, 7594 (1989).
- [8] H. E. Watson and K. L. Ramaswamy, *Proc. R. Soc. London, Ser. A* **156**, 144 (1936).
- [9] C. J. Jameson and P. W. Fowler, *J. Chem. Phys.* **85**, 3432 (1985).
- [10] S. Y. Liu and C. E. Dykstra, *J. Phys. Chem.* **91**, 1749 (1987).
- [11] J. E. Bloor and J. Yu, *J. Phys. Chem.* **94**, 5586 (1990).
- [12] M. Stählerin, C. R. Moylan, D. M. Burland, A. Willets, J. E. Rice, D. P. Shelton, and E. A. Donley, *J. Chem. Phys.* **98**, 5595 (1993).
- [13] M. Duran, Y. Yamaguchi, R. B. Remington, and H. F. Schaefer, *Chem. Phys.* **122**, 201 (1988).
- [14] P. W. Fowler and G. H. F. Diercksen, *Chem. Phys. Lett.* **167**, 105 (1990).
- [15] A. Rizzo, T. Helgaker, K. Ruud, A. Barszczewicz, M. Jaszunski, and P. Jørgensen, *J. Chem. Phys.* **102**, 8953 (1995).
- [16] G. Maroulis and C. Pouchan, *Theor. Chim. Acta* **93**, 131 (1996).
- [17] D. C. Hanna, M. A. Yuratich, and D. Cotter, *Nonlinear Optics of Atoms and Molecules* (Springer, Berlin, 1979).
- [18] Y. R. Shen, *Principles of Nonlinear Optics* (Wiley, New York, 1984).
- [19] N. F. Lane, *Rev. Mod. Phys.* **52**, 29 (1980).
- [20] *Phenomena Induced by Intermolecular Interactions*, edited by G. Birnbaum (Plenum, New York, 1985).
- [21] C. E. Dykstra, *J. Am. Chem. Soc.* **112**, 7540 (1990).
- [22] C. E. Dykstra, *J. Phys. Chem.* **94**, 180 (1990).
- [23] K. L. C. Hunt, Y. Q. Liang, and S. Sethuraman, *J. Chem. Phys.* **89**, 7126 (1988).
- [24] B. Yang, D. E. Sullivan, B. Tjijto-Margo, and C. G. Gray, *J. Phys. F* **3**, 109 (1991).
- [25] A. Elliasmine, J.-L. Godet, Y. Le Duff, and T. Bancewicz, *Mol. Phys.* **90**, 147 (1997).
- [26] *Collision and Interaction Induced Spectroscopy*, edited by G. C. Tabisz and N. Neuman (Kluwer, Dordrecht, 1995).
- [27] *Strategies and Applications in Quantum Chemistry*, edited by Y. Ellinger and M. DeFranceschi (Kluwer, Dordrecht, 1996).
- [28] A. A. Hasanein, *Adv. Chem. Phys.* **85**, 415 (1993).
- [29] D. M. Bishop, *Adv. Quantum Chem.* **25**, 1 (1994).
- [30] Y. Luo, H. Agren, P. Jørgensen and K. V. Mikkelsen, *Adv. Quantum Chem.* **26**, 165 (1995).
- [31] J. Olsen and P. Jørgensen, in *Modern Electronic Structure Theory*, edited by D. R. Yarkony (World Scientific, London, 1995), p. 857.
- [32] R. J. Bartlett and H. Sekino, in *Nonlinear Optical Materials: Theory and Modeling*, edited by S. P. Karna and A. T. Yeats, ACS Symposium Series No. 628 (ACS, Washington, D.C., 1996), p. 23.
- [33] G. Maroulis, *J. Phys. Chem.* **100**, 13 466 (1996).
- [34] A. D. Buckingham, *Adv. Chem. Phys.* **12**, 107 (1967).
- [35] A. D. McLean and M. Yoshimine, *J. Chem. Phys.* **47**, 1927 (1967).
- [36] G. Maroulis, *J. Phys. B* **26**, 2957 (1993).
- [37] G. Maroulis, *Chem. Phys. Lett.* **199**, 244 (1992).
- [38] G. Maroulis and D. M. Bishop, *Chem. Phys.* **96**, 409 (1985).
- [39] G. Maroulis, *Chem. Phys. Lett.* **199**, 250 (1992).
- [40] J. Paldus and J. Cizek, *Adv. Quantum Chem.* **9**, 105 (1975).
- [41] R. J. Bartlett, *Annu. Rev. Phys. Chem.* **32**, 359 (1981).
- [42] A. Szabo and N. S. Ostlund, *Modern Quantum Chemistry* (McMillan, New York, 1982).
- [43] S. Wilson, *Electron Correlation in Molecules* (Clarendon, Oxford, 1984).
- [44] K. Raghavachari, G. W. Trucks, J. A. Pople, and M. Head-Gordon, *Chem. Phys. Lett.* **157**, 479 (1987).
- [45] M. Urban, I. Cernusak, V. Kellö, and J. Noga, *Methods Comp. Chem.* **1**, 117 (1987).
- [46] J. D. Watts, J. Gauss, and R. J. Bartlett, *Chem. Phys. Lett.* **200**, 1 (1992).
- [47] T. H. Dunning, *J. Chem. Phys.* **53**, 2383 (1970).
- [48] H. Partridge, NASA Technical Memorandum No. 89449, 1987 (unpublished).
- [49] H. Partridge, NASA Technical Memorandum No. 101044, 1989 (unpublished).
- [50] T. H. Dunning and P. J. Hay, in *Methods of Electronic Structure Theory*, edited by H. F. Schaefer (Plenum, New York, 1987), p. 1.
- [51] G. Winnewisser, A. G. Maki, and D. R. Johnson, *J. Mol. Spectrosc.* **39**, 149 (1971).
- [52] G. Strey and I. M. Mills, *Mol. Phys.* **26**, 129 (1973).
- [53] M. J. Frisch, J. S. Binkley, H. B. Schlegel, K. Raghavachari, C. F. Melius, R. L. Martin, J. J. P. Stewart, F. W. Bobrowicz, C. M. Rohlfing, L. R. Kahn, D. J. Defrees, R. Seeger, R. A. Whiteside, D. J. Fox, E. M. Fleuder, and J. A. Pople, GAUSSIAN 86 (Carnegie-Mellon Quantum Chemistry Publishing Unit). M. J. Frisch, G. W. Trucks, M. Head-Gordon, P. M. W. Gill, M. W. Wong, J. B. Foresman, B. G. Johnson, H. B. Schlegel, M. A. Robb, E. S. Replogle, R. Gomperts, J. L. Andres, K. Raghavachari, J. S. Binkley, C. Gonzalez, R. L. Martin, D. J. Fox, D. J. Defrees, J. Baker, J. J. P. Stewart, and J. A. Pople, GAUSSIAN 92 (Revision C) (Carnegie-Mellon Quantum Chemistry Publishing Unit).
- [54] The sign of the first dipole hyperpolarizability is unambiguously defined by definition [Eq. (1)] and the given molecular orientation. In experimental determinations [see the careful analysis by X. Ward and X. Miller, *Phys. Rev. A* **19**, 826 (1979)] the sign of the measured quantity $\mu\chi^{(2)}$ is also unambiguously determined and its sign is ascribed (term used by Ward and Miller) to $\chi^{(2)}$. Confusion is easily avoided in comparisons of theoretical predictions to experimentally determined values.
- [55] C. E. Dykstra, S. Y. Liu, and D. J. Malik, *Adv. Chem. Phys.* **75**, 37 (1989).
- [56] M. Grayson and W. T. Raynes, *Chem. Phys. Lett.* **214**, 473 (1993).
- [57] See Spackman's discussion, in Ref. [7], p. 7600.