J. Phys. Chem. A **2009,** *113,* 2615–2622 **2615**

Axial Asymmetry of the Charge- and Spin-Density Distributions in Π States. Molecular Quadrupole Moments and Hyperfine Coupling Constants of CH, NH, OH, CF, LiO, NO, and FO

Pablo J. Bruna and Friedrich Grein*

Department of Chemistry and Centre for Laser, Atomic and Molecular Sciences (CLAMS), University of New Brunswick, Fredericton, New Brunswick, Canada E3B 5E3

Received: September 5, 2008; Revised Manuscript Received: December 11, 2008

The axial *asymmetry* of the charge- and spin-density distributions in Π states is studied via second-rank traceless tensors P_{ii} ($ii = xx, yy, zz$), namely, quadrupole moments (Θ_{ii}), electric field gradients (q_{ii}), and magnetic dipolar (T_{ii}) hyperfine coupling constants (hfcc's). In linear molecules, it holds that $P_{xx} \neq P_{yy} \neq P_{zz}$ for Π, but $P_{xx} = P_{yy} \neq P_{zz}$ for Σ, Δ, Φ,..., states. Thus, *traceless* P_{ii} in Π states have two independent parameters, $P_{\|} = P_{zz} \propto [r^m(3\cos^2\theta - 1)]$ and $\delta P_\perp = |P_{xx} - P_{yy}| \propto [r^m \sin^2\theta]$, with $m = 2(\Theta_{ii})$ or $-3(q_{ii}, T_{ii})$. All linear states have $P_{\|} \neq 0$, but only Π states exhibit $\delta P_\perp \neq 0$, as shown by hfcc's like $c = (3/2)T_{zz}$, and $d = |T_{xx} - T_{yy}|$, as well as $q_0 = (-q_{zz})$ and $|q_2/2| = |q_{xx} - q_{yy}|$. Little is known about Θ_{zz} and $\delta\Theta_\perp = |\Theta_{xx} - \Theta_{yy}|$ in Π states since most experimental values (gas-phase) are rotational averages, and several theoretical studies have reported Θ_{zz} but assumed $\delta\Theta_\perp = 0$. The diatomics studied here have $X^2\Pi_{1/2}(\pi^1)$ ground states, like CH and NO, or are of type $X^2\Pi_{3/2}(\pi^3)$, like OH, CF, LiO, and FO. The $A^3\Pi(\sigma\pi^3)$ state of NH is also included. Our $P_{\|}$ and $\delta P_\perp$ values—calculated at the experimental R_e's with the B3LYP/aug-cc-pVQZ method—reproduce well the available literature data. The properties of the CF and FO radicals are not well-known so that our {c, d} and {q_0, q_2} values should help future experimental studies of their hyperfine spectra. Excluding OH, the complete quadrupole sets {Θ_{zz}, $\delta\Theta_\perp$} are new for all species discussed here. For comparison purposes, Θ_{zz} of a low-lying Σ state is also calculated for each $X^2\Pi$ radical.

I. Introduction

The *axially asymmetric* charge- and spin-density distributions (CDD and SDD) of linear radicals in electronic Π states are studied via three second-rank traceless tensorial properties P_{ii} ($ii = xx, yy, zz$). One property describes the interaction between spin dipoles, as given by T_{ii}(X), the magnetic dipolar hyperfine coupling constant (hfcc) for nucleus X.[1] The other two are electric properties: (1) the electric field gradient (efg) parameter q_{ii}(X), related to the nuclear quadrupole coupling constant $\chi_{ii} = eQq_{ii}$(X),[2] Q = *nuclear* quadrupole moment, and (2) the *molecular* quadrupole moment Θ with Cartesian components Θ_{ii}.[3] The quantum mechanical operators for $P_{ii} = T_{ii}, q_{ii}, \Theta_{ii}$ behave equally with respect to (the symmetry operation of) rotation about the molecular axis z.[4]

We have recently determined[4] how many independent parameters (n) are needed to describe the electric 2^l-pole moments ($\equiv$ **P**) of linear radicals in different electronic states, i.e., whether the corresponding CDDs are fully described by one ($P_{\|}$) or two ($P_{\|}$, $\delta P_\perp$) anisotropies: Σ states have $n = 1$ ($P_{\|}$) for all l-values, whereas Π states have $n = 2$ ($P_{\|}$, $\delta P_\perp$) for $l \geq 2$ (quadrupole Θ and higher multipoles). Interestingly, Δ states show a mixed behavior, with $n = 1$ for $l = 1, 2, 3$ but $n = 2$ for $l \geq 4$.

In general, measured gas-phase multipole moments are rotational averages, i.e., the asymmetry of the CDD in Π states ($\Theta_{xx} \neq \Theta_{yy} \neq \Theta_{zz}$) cannot be verified. As well, experimental multipoles are scarce for Π states.[3] Thus, other traceless second-rank $P_{ij} = T_{ii}$, q_{ii} properties—amenable to experiments and free of rotational averaging—have to be considered which provide direct evidence about the difference in CDD/SDD symmetries in Σ and Π states. According to the literature on NO and OH ($X^2\Pi$), for example, two dozen theoretical papers[5,6] studied one or several of the P_{ii} (T_{ii}, q_{ii}, Θ_{ii}) properties but only 10 reported both $P_{\|}$ and $\delta P_\perp$. Experimentally,[1] the {$c = 3T_{\|}/2$, $d = \delta T_\perp$} hfcc's indicate axially *asymmetric* SDDs, e.g., in MHz, {−59, 113} for ^{14}NO and {221, −429} for ^{17}OH. The same applies to triplet states, with values of {15, 66} for ^{14}NH ($A^3\Pi$)[7] and {16, 213} for ^{13}CO ($a^3\Pi$).[8] Further, the {$\chi_0(P_{\|})$, $\chi_2(\delta P_\perp)$} parameters, in MHz, are {−2, 24} for ^{14}NO and {−2, 66} for ^{17}OH.[1] Throughout, both d and χ_2 clearly dominate the hfcc's so that works neglecting $\delta P_\perp$ do not correctly describe Π states.

In the present paper we present calculations on both $P_{\|}$ and $\delta P_\perp$ [$\mathbf{P} \equiv \mathbf{T}, \mathbf{q}, \mathbf{\Theta}$] for six $X^2\Pi$ diatomics (CH, NO, OH, LiO, CF, FO)[9–14] and $A^3\Pi$ of NH.[7] The $\delta\Theta_\perp$ anisotropies are new for all species, except for OH. This paper is organized as follows: section II deals with the general properties of $P_{\|}$ and $\delta P_\perp$, whereas section III presents our results. The whole material of this work is, respectively, discussed and summarized in sections IV and V.

II. Second-Rank Tensor Properties: Anisotropies

II.A. General Definitions. First we clarify our nomenclature regarding tensors for linear molecules ($C_{\infty v}$, $D_{\infty h}$). The molecule-fixed system of coordinates is used throughout (z = molecular axis, and $ii = xx, yy, zz$). We associate three equivalent types of tensors to a given second-rank property:

(i) Cartesian tensor C_{ii} (second moments). Linear molecules have three nonzero components, $C_{ii} \equiv \{x^2, y^2, z^2\}$ for Θ_{ii}, or $C'_{ii} \equiv \{x^2/r^5, y^2/r^5, z^2/r^5\}$ for hfcc's, with $r^5 = (x^2 + y^2 + z^2)^{5/2}$.

---

* Corresponding author. Phone: +1-506-453-4776. Fax: +1-506-453-4981. E-mail: fritz@unb.ca.

10.1021/jp807885c CCC: $40.75

Here, $\sum C_{ii} = r^2$ and $\sum C'_{ii} = r^{-3}$, that is, both C_{ii} and C'_{ii} are *traced* tensors. Since either $x^2 = y^2 \neq z^2$ or $x^2 \neq y^2 \neq z^2$, the number (n) of independent components is 2 or 3, respectively;

(ii) tensor P_{ii} (P'_{ii}) with linear combinations of Cartesian C_{ii} (C'_{ii})'s satisfying the *traceless* condition $\sum P_{ii} = (P_{xx} + P_{yy} + P_{zz}) = 0$. Here, description of axially *symmetric* and *asymmetric* DDs with P_{ii} (P'_{ii}) tensors requires $n = 1$ and 2 parameters, respectively. Typical P_{ii} examples are the quadrupole terms $\Theta_{xx} = (3x^2 - r^2)/2$, $\Theta_{yy} = (3y^2 - r^2)/2$, and $\Theta_{zz} = (3z^2 - r^2)/2$ [Buckingham's definition].[3] Note that each Cartesian component P_{ii} (Θ_{ii}) or P'_{ii} (T_{ii}, q_{ii}) is defined using the same formula;

(iii) irreducible tensors $P_0^{(0)}$ and $P_m^{(2)}$, the latter with two nonzero components, $P_0^{(2)}$ and $P_{|2|}^{(2)}$ [$\equiv$ Re($P_{\pm 2}^{(2)}$)].[4,15] The *isotropic* part of any second-rank tensor consists of the trace, e.g., $P_0^{(0)} \propto r^2$ for the molecular quadrupole. Only for traced tensors is $P_0^{(0)}$ of interest, e.g., $P_0^{(0)} \equiv \langle \alpha \rangle = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3$ for the polarizability. Further, $P_0^{(2)}$ is proportional to P_{zz}, whereas the perpendicular anisotropy is $P_{|2|}^{(2)} = |P_{xx} - P_{yy}|$. Taking again the quadrupole as an example, its irreducible $P_m^{(2)}$ parts are $P_0^{(2)} \equiv \Theta_0^{(2)} = \Theta_{zz} = (3z^2 - r^2)/2$ and $P_{|m|}^{(2)} \equiv \Theta_{|2|}^{(2)} = |\Theta_{xx} - \Theta_{yy}| = (3/2)|x^2 - y^2|$.

Each of the C_{ii}, P_{ii}, and $P_m^{(l)}$ sets has practical applications. Ab initio calculations on linear molecules are carried out in the lower C_{2v}/D_{2h} symmetry, with C_{ii}/C'_{ii} being calculated first and thereafter transformed to P_{ii}/P'_{ii}'s. The C_{ii}, C'_{ii} sets are not symmetry adapted with respect to the $C_{\infty v}/D_{\infty h}$ point groups. For the P_{ii} set, only $P_{zz} \equiv P_0^{(2)}$ is symmetry adapted ($\Sigma^+_{(g)}$).[4] The component $P_{\pm 2}^{(2)} \propto [(P_{xx} - P_{yy}) \pm 2iP_{xy}]$ transforms like doubly degenerate $\Delta_{(g)}$.[4] In C_{2v} symmetry, the Re and Im parts of $P_{\pm 2}^{(2)}$ transform as A_1 (totally symmetric) and A_2, respectively. Here, we work exclusively with the A_1 component, written as the absolute value $|P_{xx} - P_{yy}| = P_{|2|}^{(2)}$.

Summing up, the whole process starts with C_{ii} $\{C_{xx}, C_{yy}, C_{zz}\}$, a Cartesian set physically sound to describe linear species but inadequate to use in conjunction with group theory. In going from $\{C_{ii}\}$ to $\{P_0^{(0)}, P_m^{(2)}\}$, the C_{ii} set is decomposed into one *isotropic* $P_0^{(0)}$ and two *anisotropic* parts $P_m^{(2)}$ ($|m| = 0, 2$), one parallel and the other perpendicular to the molecular axis.[15]

II.B. Parallel Anisotropy ($P_{||}$). There exist several definitions of the second-rank anisotropies.[3,4,16−18] The parallel anisotropy $P_{||}$, in polar (eqs 1a−1b′) and in Cartesian coordinates (eqs 1b′−1e) read as

$$P_{||} = P_{zz} = P_0^{(2)}$$

$$= k(r)[(3\cos^2\theta_z - 1)/2] = k(r)[2(\pi/5)^{1/2} Y_0^{(2)}(\theta_z, \phi_z)] \tag{1a,1a′}$$

$$= k(r)[L_0^{(2)}(\cos\theta_z)] = k(r)[L_0^{(2)}(z/r)] \tag{1b,1b′}$$

$$= k(r)[r^{-2}\{3z^2 - r^2\}/2] \tag{1c}$$

$$= k(r)[r^{-2}\{(z^2 - x^2) + (z^2 - y^2)\}/2] \tag{1d}$$

$$= k(r)[r^{-2}\{(z^2 - (x^2 + y^2)/2\}] \tag{1e}$$

Here, r = distance with respect to the chosen origin; $Y_0^{(2)}(\theta_z, \varphi_z)$ = spherical harmonics $Y_m^{(2)}$ for $m = 0$; and $L_0^{(2)}(\alpha) = (3\alpha^2 - 1)/2$, the associated Legendre polynomial $L_m^{(l)}(\alpha)$. As shown by eqs 1a, 1b, an irreducible tensor transforms under rotations as the corresponding spherical harmonics.[15]

Equations 1a−1e apply to each $P_{ii} = T_{ii}$, q_{ii}, Θ_{ii}. Which of them is under consideration is specified by the factor $k(r)$ composed of appropriate constants and/or radial functions (other than r^{-2}). For example, in $^2(\Sigma, \Pi)$ states the hyperfine parameter c [$= (3/2)T_{zz}$] has $k(r) = 2r^{-3}$ if one works with atomic units but $k(r) = (g_e g_n \mu_B \mu_N) \times 2r^{-3}$ with MHz units.[1,18] As another example, Buckingham[3] defines the quadrupole $\Theta_{zz} = r^2[(3\cos^2\theta_z - 1)/2]$ so that $k(r) = r^2$. However, Hirschfelder et al.[16] define such component as $\Theta'_{zz} = r^2[(3\cos^2\theta_z - 1)] = 2\Theta_{zz}$ so that now $k(r) = 2r^2$.

Equations 1a−1e give insights about the symmetry features of P_{zz}. Equation 1a shows that P_{zz} only depends on the polar angle θ, i.e., on the projection onto the z-axis. Moreover, $P_{zz}/k(r)$ exhibit following properties: (i) a maximum value of 1 along z, (ii) a minimum of $-1/2$ in the xy-plane, and (iii) nodal surfaces for $\cos\theta$ = sqrt(1/3), or $\theta = 54°44'$ (like as in d_σ-orbitals). In short, the operator P_{zz} (eq 1a) is *positive* for θ ranging from about $-55°$ to $55°$ for both $+z$ and $-z$ directions, but *negative* between about 55° and 125° (and from about $-235°$ to $-305°$).

The description above—with the lobe signs $(+)_z(-)_{xy}(+)_z(-)_{xy}$ counted anticlockwise—only applies for positive $k(r)$. For instance, the electronic contribution to Θ is *negative* and the lobe's scheme becomes $(-)_z(+)_{xy}(-)_z(+)_{xy}$. The positive nuclear contribution only affects Θ_{zz}. Thus, a prolate-shaped CDD has a *negative* Θ_{zz}, whereas an oblate-shaped has a *positive* Θ_{zz}. In chemical language, a prolate structure reveals the σ-density to be more extended spatially (along z) than the π-density (xy-plane); conversely, an oblate distribution ($\Theta_{zz} > 0$) unveils a predominant π-density.[19]

Equations 1c−1e are the expressions used in ab initio packages. Equation 1c shows that P_{zz} vanishes for spherical symmetry, where $x^2 = y^2 = z^2 = r^2/3$. This never happens in linear molecules, which are either axially symmetric ($x^2 = y^2 \neq z^2$) or asymmetric ($x^2 \neq y^2 \neq z^2$). According to eq 1d, P_{zz} ($P_{||}$) is proportional to $[(z^2 - x^2) + (z^2 - y^2)]$, the sum of two basic anisotropies, ($z^2 - x^2$) and ($z^2 - y^2$). Further, eq 1e shows that $P_{zz} \propto [z^2 - (x^2 + y^2)/2]$, where z^2 is being compared against the average $(x^2 + y^2)/2$.

II.C. Perpendicular Anisotropy, $\delta P_\perp \propto |P_{xx} - P_{yy}|$. The perpendicular components P_{xx} and P_{yy} are

$$P_{xx} = k(r)[(3\cos^2\theta_x - 1)/2] = k(r)[r^{-2}\{3x^2 - r^2\}/2] \tag{2}$$

$$P_{yy} = k(r)[(3\cos^2\theta_y - 1)/2] = k(r)[r^{-2}\{3y^2 - r^2\}/2] \tag{3}$$

Here, $\cos\theta_x$ and $\cos\theta_y$ are direction cosines. Since $\sum P_{ii} = 0$, the relation $P_{zz} = -(P_{xx} + P_{yy})$ is obeyed by all electronic states. Only for symmetric CDD/SDDs it holds $P_{xx} = P_{yy}$, or equivalently, $P_{xx} = P_{yy} = -P_{zz}/2$. The *perpendicular* anisotropy $\delta P_\perp$ [$\propto P_{|2|}^{(2)}$] is defined[4] as

$$\delta P_\perp = |P_{xx} - P_{yy}| = |k(r)[(3/2)r^{-2}\{x^2 - y^2\}]| \tag{4a}$$

$$= |k(r)[(3/2)\{\sin^2\theta(\cos^2\phi - \sin^2\phi)\}]| \tag{4b}$$

$$= |k(r)[(3/2)\{\sin^2\theta\cos 2\phi\}]| \tag{4c}$$

where φ = azimuthal angle. The factor $\cos 2\varphi$ assures that $\langle\psi_{\Lambda=+1}|\sin^2\theta\cos 2\varphi|\psi_{\Lambda=-1}\rangle$ is nonzero only for Π states.[4] The operator eq 4a has the same functional dependency as an atomic $d_\delta[d_{(x^2-y^2)}]$ orbital, where again the four lobes alternate their signs as (+)(−)(+)(−), or similar cyclic variations.

III. Results

Cartesian components for T_{ii}, q_{ii}, and Θ_{ii} are calculated with GAUSSIAN03,[20] using the B3LYP/aug-cc-pVQZ method. Electric and magnetic properties are evaluated with CDDs and SDDs, respectively. The origin of coordinates lies at atom X for hfcc's, and at the center of mass for Θ_{ii}. These first-order properties are calculated as expectation values, $\langle P\rangle = \int P(\Psi_\Lambda{}^*\Psi_\Lambda)\,d\tau$, where Ψ_Λ is the electronic wave function of a given Λ state. The results are first presented for T_{ii} (best studied

TABLE 1: Magnetic Hyperfine Coupling Constants for H, Li, and C Atoms in the $X^2\Pi$ Radicals CH, OH, LiO, and CF, as Well as $A^3\Pi$ of NH[a,b,c]

X	XY	ref	c $(3/2T_{zz})$	d $\|T_{xx} - T_{yy}\|$	b_F	b	a'	a
H	CH(π^1)	tw	0.110	0.081	−0.010	−0.047	0.118	
	expt	9e	0.107	0.082	−0.013	−0.049	0.118	0.102
		9b	0.109	0.082	−0.013	(−0.049)	0.118	0.102
		6l	0.109	0.070	−0.012	(−0.046)	0.106	0.103
		9c	0.111	(0)	−0.012	(−0.049)		
		9d	0.109	(0)	−0.012	(−0.048)		
	OH(π^3)	tw	0.249	0.106	−0.014	−0.097	0.189	
	expt	6a	0.250	0.106	−0.017	(−0.100)	0.189	0.161
	expt	11c, d	0.245	0.106	−0.016	(−0.098)	0.188	0.162
		9b	0.245	0.106	−0.016	(−0.098)	0.188	0.163
		6i	0.249	0.108	−0.016	(−0.099)		0.165
		6l	0.250	0.090	−0.018	(−0.101)	0.173	0.164
		6b	0.259	0.071			0.157	0.158
		9d	0.244	(0)	−0.014	(−0.095)		
	NH($\sigma\pi^3$)	tw	0.185	0.049	0.067	0.005	0.111	
	expt	7	0.170	0.049	0.067	0.010	0.106	0.139
		9b	0.172	0.057	0.067	0.010	0.114	0.126
		6l	0.183	0.039	0.070	0.009	0.100	0.132
Li	LiO(π^3)	tw	0.068	0.018	−0.009	−0.032	0.041	
	expt	12a	0.068	0.019	(−0.086)	−0.109	0.042	0.039
	expt	12b	(0.074)	0.009	(−0.070)	−0.095	0.034	0.029
C	CH(π^1)	tw	−1.017	2.104	0.025	0.364	1.765	
	expt	9e	−0.977	2.055	0.037	(0.363)	1.729	1.626
		9a	−0.969	1.940		(0.323)	1.617	1.614
		9b	−0.977	2.061	0.033	(0.359)	1.735	1.640
		6l	−0.959	1.918	0.011	(0.331)	1.599	1.599
		9c	−0.951	(0)	0.032	(0.349)		
		9d	−0.852	(0)	0.004	(0.288)		
	CF(π^3)	tw	−1.114	2.163	0.041	0.412	1.792	

[a] $c = (3/2)\langle(3\cos^2\theta - 1)/r^3\rangle_{SD}$; $d = (3/2)\langle 3\sin^2\theta/r^3\rangle_{SD}$; $b_F = (8\pi/3)|\psi_\Lambda(0)|^2_{SD}$; $b = b_F - c/3$; $a' = d + c/3$; $a = 2\langle r^{-3}\rangle_{CD}$ (refs 1 and 18). SD and CD stand for spin- and charge-density distributions. [b] Values given in parentheses were here derived using published information. d = (0) indicates the original article does not report this parameter. [c] All data in atomic units.

experimentally), then for q_{ii} (less known), and finally for Θ_{ii} (mostly theoretical data). All results are in atomic units (au), i.e., independent of isotopic species for hfcc's. The equilibrium distances[21] used are (in angstroms): 1.1199/1.085 for CH, 1.0362/1.037 for NH, 0.9697/1.0121 for OH, 1.688/1.589 for LiO, 1.1508/1.318 for NO, 1.2667/1.327 for CF, and 1.354/1.80 for FO (first value for the ground state; second for the excited state used in the quadrupole calculations).

III.A. Magnetic Dipolar Term c $[3T_{zz}/2]$ and Perpendicular Anisotropy d $[T_{xx} - T_{yy}]$. Magnetic hfcc's are reported as A_{iso} and A_{dip} $[T_{xx}, T_{yy}, T_{zz}]$ in theoretical works;[22] by a, b, c, d in spectroscopy;[1,18] and by $A_{\|}$, $A_{\perp}$ in EPR studies.[1b] Relevant equivalencies are $A_{iso} = b_F = (b + c/3) = (A_{\|} + A_{\perp})/3$, $A_{dip} = c/3 = T_{zz}/2 = (A_{\|} - A_{\perp})/3$, $A_{\|} = (b + c) = (A_{iso} + 2A_{dip})$, $A_{\perp} = b = (A_{iso} - A_{dip})$, and $d = (T_{xx} - T_{yy})$. Tables 1 and 2 list the calculated values of c and d, together with literature data (the magnetic hfcc's a, a', b_F, and b are also given; see Table 1 for definitions). The two magnetic anisotropies are[1,18]

$$T_{\|}:\quad c = [(36\pi/5)^{1/2}]K\langle\Lambda_{+1}|r^{-3}\cdot Y_0^{(2)}(\theta,\phi)|\Lambda_{+1}\rangle_{SD} = (3/2)K\langle r^{-3}\cdot(3\cos^2\theta - 1)\rangle_{SD} \quad (5)$$

$$\delta T_{\perp}:\quad d = -[(24\pi/5)^{1/2}]K\langle\Lambda_{+1}|r^{-3}\cdot Y_0^{(2)}(\theta,\phi)|\Lambda_{-1}\rangle_{SD} = -(3/2)K\langle\Lambda_{+1}|r^{-3}\cdot\sin^2\theta\cdot e^{i2\phi}|\Lambda_{-1}\rangle_{SD} \quad (6a)$$

$$\propto (3/2)K\langle r^{-3}\cdot\sin^2\theta\rangle_{SD}\}^{\#} \quad (6b)$$

Here, $K = 1$. We find $\delta T_{\perp}$ from eq 6b—a common definition in the literature, here labeled as #— to be somewhat misleading since (1) as written, $\langle r^{-3}\cdot\sin^2\theta\rangle$ can only be positive, although experimentalists sometimes report negative expectation values for this anisotropy, and (2) it ignores that the perpendicular anisotropy also depends on the azimuthal angle φ. The other two definitions are mathematically sound, as they explicitly show a φ dependency via the phase-factor $e^{i2\varphi}$.[23]

Our results are analyzed below and compared with literature data. In general terms, the B3LYP/aug-cc-pVQZ calculations reproduce within 10%, or better, all literature data known to us. Prior theoretical values of the two dipolar anisotropies c, d have only been reported for CH, NH, and OH.[6i,9b] Further, two ab initio papers on NO,[5a,e] and one on CF,[13a] reported c but not d.

The parameter $a' = [c/3 + d]$ describes the isotropic average $\langle 1/r^3\rangle_{SDD}$, to be compared with $a \propto \langle 1/r^3\rangle_{CDD}$. Both averages differ by no more than 10%.[1c,24] Since $P_{xx,yy} = (-P_{zz} \pm \delta P_{\perp})/2$, the Cartesian T_{ii}'s are $T_{xx} = (-c/3 + d/2)$ and $T_{yy} = (-c/3 - d/2)$, together with $T_{zz} = 2c/3$.

III.A.1. H in CH, OH, and NH, and Li in LiO. All magnetic hfcc's for the s-type atoms H and Li are small (below 0.25 au, Table 1). The electric dipole moments μ_e for the $X^2\Pi$ hydrides MH give charge distributions $M^{\delta-}H^{\delta+}$ indicating little charge (spin) density at H. Also, the $X^2\Pi$ states do not have singly occupied σ-MOs [$(2\sigma^2 1\pi)$ for CH, $(2\sigma^2 1\pi^3)$ for OH], thus resulting in small and negative b_F(H)'s, −0.010 to −0.017 au. Taking an isotropic $b_F = 0.318$ au as reference for H(s), both CH and OH have average H(1s) SDDs below 5%. The same picture applies to LiO [$X^2\Pi(\sigma^2\pi^3)$], with a strong ionic character Li^+O^- ($\mu_e \approx 6$ D), and a Li(2s) spin density lying around 4%.

The dipolar components c(Y) and d(Y) [Y = H, Li] are throughout small in these MH and LiO radicals—as expected for atoms without valence [H] or quite-diffuse p-AOs [Li]. The spin anisotropy around H/Li is actually being "induced" by the more compact valence p-AOs from neighboring centers. The longitudinal anisotropy c(Y) is somewhat larger than the perpendicular d(Y) (Table 1). The remaining Π radicals XY show the opposite trend (see below).

$A^3\Pi(2\sigma 1\pi^3)$ of NH with σ and π open shells has $b_F(H) = 0.067$ au (299 MHz), giving an s(H) spin density of ca. 20%. Experimental and theoretical data are well reproduced (Table 1).

III.A.2. C in CH and CF. Both CH and CF have $X^2\Pi(\pi^1)$ ground states. The single π-electron is a pure $2p_\pi$(C) species in CH but a delocalized MO [$2p_\pi$(C) + $2p_\pi$(F)] in CF. Inspection of Table 1 reveals three features: (i) the π open shell invariably gives a positive perpendicular anisotropy d(C) but a negative longitudinal anisotropy c(C), (ii) the parameter d(C) is about twice as large as $|c(C)|$, and (iii) the pair $\{c(C), d(C)\}$ has practically the same magnitude in both CH and CF. Pictorially, these trends indicate that the C, N, O, and F centers in these $X^2\Pi$ radicals exhibit oblate-shaped SDDs.

III.A.3. N in NO and NH. The general trends are maintained in NO, with d(N) positive and larger than $|c|$. The same applies to d(N) in NH, but now $c(N) > 0$ due to a $\sigma\pi^3$ open shell. Accordingly, the Fermi contact term b_F(N) in NH($A^3\Pi$) is substantially larger than for all other diatomics in Tables 1 and 2.

III.A.4. O in OH, LiO, NO and FO. Except for NO, the O atom carries most of the SDD in all other O-containing species (Table 2), namely, $\{c; d\}_O$ amounts to $\{-1.3; 2.9$ au$\}$ in NO but on average about $\{-2.9; 5.9$ au$\}$ in OH, LiO, and FO.

III.A.5. F in CF, FO. The existence of an oblate SDD, with $c(F) < 0$, and smaller in magnitude than $d(F) > 0$, is maintained in CF and FO. Theory and experiment agree that F carries more SD in FO than in CF.

III.B. Electric Field Gradient (q_{zz}) and Perpendicular Anisotropy $\delta q_\perp = (q_{xx} - q_{yy})$. According to Western et al.,[10d] the two efg quantities reported by experimentalists are

$$q_{\|}:\quad q_0 = \left\langle \Lambda = +1 \middle| \sum\nolimits_i e_i r_i^{-3} \cdot (3\cos^2\theta_{iz} - 1) \middle| \Lambda = +1 \right\rangle_{\mathrm{CD}} \tag{7}$$

$$[2\delta q_\perp]:\quad q_2 = \left\langle \Lambda = +1 \middle| \sum\nolimits_i e_i r_i^{-3} \cdot 3\sin^2\theta_{iz} \cdot \mathrm{e}^{i2\phi}) \middle| \Lambda = -1 \right\rangle_{\mathrm{CD.}} \tag{8}$$

The sum runs over all charged particles, except the nucleus under consideration. For XY, the nuclear contribution to q_{zz}(X) due to atom Y is $[q_{zz}]_Y = 2Z_Y/R^3$. The label CD points out that these matrix elements are calculated with CDDs. Equation 8 with the factor $e^{i2\varphi}$ is the correct definition, whereas many articles/textbooks give $q_2 = \langle\Lambda_{+1}|\sum_i e_i r_i^{-3} \cdot 3\sin^2\theta_{iz}|\Lambda_{-1}\rangle^{\#}$. In our nomenclature, $q_0 \equiv q_{zz}$ and $q_2 \propto |q_{xx} - q_{yy}|$. Experimentally,[5i,25] $|q_2| = 2|q_{xx} - q_{yy}|$ so that we report our results as $q_2' = |q_{xx} - q_{yy}|$. Thus, the Cartesian efg components are $q_{zz} = q_0$, $q_{xx} = [-q_0/2 + \delta q_\perp/2]$, and $q_{yy} = [-q_0/2 - \delta q_\perp/2]$, with $\delta q_\perp = q_2' = |q_2/2|$. Table 3 summarizes our results, together with literature data. Previous theoretical efg's for both atoms in CH,[6c,9a] and OH,[6c,d] and for O in NO,[5h,6j] omitted the leading term $\delta q_\perp$.

Experimental (q_0) and our theoretical (q_{zz}) values are of similar magnitude but opposite signs, i.e., B3LYP/aug-cc-pVQZ, give quite reliable efg values (like as for dipolar hfcc's). For atoms different than H or Li, the relative magnitude between q_0 and $\delta q_\perp$ is the same as for the magnetic c and d parameters: the perpendicular component predominates by large (see also section IV).

Experiment and theory disagree when reporting $\delta q_\perp$. We calculate $\delta P_\perp \propto \langle \sin^2\theta \cdot e^{2i\varphi}/r^3 \rangle$ in exactly the same manner for $P = T_{ii}$ and q_{ii}. Tables 1 and 2 do not show any discrepancy between the experimental and theoretical signs of d, but that is not the case for experimental q_2, which is negative for H in OH, Li in LiO, and O in OH, NO. Note that $q_{xx}, q_{yy} = (-q_0 \pm \delta q_\perp)/2$ so that a change in the sign of $\delta q_\perp$ only exchanges q_{xx} with q_{yy}. Curiously, experiments on NO ($X^2\Pi_r$) report $q_2(N) > 0$ but $q_2(O) < 0$ (Table 3). We point out this "anomaly" since

TABLE 2: Magnetic Hyperfine Coupling Constants for N, O, and F Atoms in the $X^2\Pi$ Radicals NO, OH, LiO, FO, and CF, as Well as $A^3\Pi$ of NH[a,b]

X	XY	ref	c (3/2T_{zz})	d $\|T_{xx} - T_{yy}\|$	b_F	b	a'	a
N	NO(π^1)	tw	−1.531	2.992	0.026	0.536	2.482	
	expt	10e, f, g	−1.525	2.917	0.069	0.577	2.409	2.181
		5a	−1.418	(0)	0.173	(0.646)		
		5e	−1.500	(0)	0.027	(0.527)		
	NH($\sigma\pi^3$)	tw	0.199	1.753	0.470	0.404	1.819	
	expt	7	0.394	1.720	0.491	0.360	1.851	2.321
		9b	0.205	2.325	0.471	0.403	2.393	2.560
		6l	0.214	1.749	0.489	0.364	1.820	2.535
O	OH(π^3)	tw	−2.977	5.992	0.010	1.002	5.000	
	expt	11a	−2.846	5.693	0.142	(1.091)	4.744	4.057
	expt	11c, d	−3.054	5.940	0.084	(1.012)	4.922	4.436
		9b	−2.900	6.029	0.064	(1.031)	5.062	4.461
		6i	−2.897	5.875	0.054	(1.020)		4.418
		6l	−2.809	5.777	0.040	(0.976)	4.841	4.419
		9d	−2.633	(0)	0.025	(0.853)		
	LiO(π^3)	tw	−2.772	5.346	−0.004	0.920	4.438	
	NO(π^1)	tw	−1.319	2.897	0.019	0.459	2.457	
	expt	10f, g	−1.290	2.850				
		5a	−1.269	(0)	0.065	(0.488)		
		5e	−1.207	(0)	0.027	(0.429)		
	FO(π^3)	tw	−2.881	5.851	0.013		4.891	
F	CF(π^1)	tw	−0.703	1.639	0.023	0.257	1.405	
	expt	13b, c	−0.703	1.578	0.036	0.536	1.344	1.406
		13a	−0.634	(0)	(0)	0.211		1.251
	FO(π^3)	tw	−1.244	2.158	0.022		1.743	
	expt	14b, c, d	−1.208	1.947	0.410	0.813	1.544	1.554

[a] See footnotes[a] and [b] in Table 1. [b] All data in atomic units.

TABLE 3: Electric Field Gradient Parameters q_{zz} and $\delta q = \lvert q_{xx} - q_{yy}\rvert$ Calculated for Selected X $^2\Pi$ Radicals at Equilibrium (NH in Its A$^3\Pi$ Excited State)[a,b]

X	XY	ref	q_{zz} $(-q_0)$	$\lvert q_{xx} - q_{yy}\rvert$ $\lvert q_2/2\rvert$
H	CH(π^1)	tw	−0.230	0.123
		6c	−0.255	(0)
		9a	−0.237	(0)
	OH(π^3)	tw	−0.426	0.090
	expt	11c, d	−0.433	0.094*
		6c	−0.186[c]	(0)
		6d	≈ −0.45	(0)
	NH($\sigma\pi^3$)	tw	−0.372	0.081
Li	LiO(π^3)	tw	0.059	0.023
	expt	12a	0.047	0.018
	expt	12b	0.047	(0)
C	CH(π^1)	tw	1.027	2.024
		6c	0.928	(0)
		9a	0.943	(0)
	CF(π^1)	tw	0.233	2.019
F[d]	CF(π^1)	tw	−1.554	1.849
	FO(π^3)	tw	−4.393	1.983
N	NO(π^1)	tw	0.478	2.703
	expt	10e, f, g	0.387	2.411
		5a	0.682	2.869
		5b	0.327	2.967
		5h	0.385	2.416
		5h	0.371	(0)
		5d	0.502	(0)
	NH($\sigma\pi^3$)	tw	−1.620	2.953
	expt	7	−1.478	2.280
O	OH(π^3)	tw	−0.281	5.146
	expt	11c, d	−0.329	5.6 ± 0.8*
		6c	0.319	(0)
		6d	−0.240	(0)
		6j	0.320	(0)
	LiO(π^3)	tw	1.632	4.304
	NO(π^1)	tw	−0.205	2.896
	expt	10e, f, g	0.223	2.70*
		5h	−0.230	(0)
		6j	0.229	(0)
	FO(π^3)	tw	−3.245	5.129

[a] Data in au. [b] Experimental $\lvert q_2\rvert$ corresponds to twice the theoretical $\lvert q_{xx} - q_{yy}\rvert$. A q_2 value tagged * indicates a negative q_2 in the original experimental article. [c] A theoretical $q_{zz} = -0.186$ au (Bender and Davidson, ref 6c) seems to be a misprint. Interpolating between their absolute values of 0.35 and 0.55 au for NH and FH, respectively, $q_H(OH) \approx -0.45$ au. [d] Experimental q's from polyatomic molecules: $q(F) = 2.7$ au in CF_4 (ref 27d), and $q(F) \approx 4.5$ au in F_2O (ref 27f). A nuclear $Q = -94.2$ mb was used for $^{19}F^*(5/2)$ to convert experimental MHz data to q (au) (ref 27g).

experimentalists argue that *regular* $^2\Pi_r(\pi^1)$ and *inverted* $^2\Pi_i(\pi^3)$ states have positive and negative q_2's, respectively.[1c,18]

The interaction between the nuclear quadrupole (Q) and the efg at a given nucleus is given by the nuclear quadrupole constant $\chi_{0,2} = eQq_{0,2}$.[10d,26] Clearly, $\chi \neq 0$ requires a nuclear quadrupole moment $Q \neq 0$, or nuclear spin $I \geq 1$. It is often assumed that nuclear quadrupole spectroscopy cannot be applied to fluorine-containing compounds because $Q[^{19}F(I = 1/2)] = 0$. However, the *nuclear* excited state $^{19}F^*(I = 5/2)$ has $Q \neq 0$, and various experimental studies have reported $q[^{19}F^*]$ for ClF, $(C_2F_4)_n$, OF_2, SiF_4, BF_3, and a series of fluorobenzenes.[27]

III.C. Molecular Quadrupole Moment (θ_{zz}) and Perpendicular Anisotropy ($\delta\theta_\Pi$). The quadrupole moment has the parallel (θ_{zz}) and perpendicular ($\delta\theta_\Pi$) anisotropies

$$\Theta_\parallel: \quad \Theta_{zz}\{\Theta_0^{(2)}\} = \left\langle \Lambda = +1 \middle| \sum_i e_i r_i^2 \cdot (3\cos^2\theta_{iz} - 1) \middle| \Lambda = +1 \right\rangle_{CD} \tag{9}$$

$$[\delta\Theta_\perp]: \quad \lvert\Theta_{xx} - \Theta_{yy}\rvert\{\Theta_{|2|}^{(2)}\} = \left\langle \Lambda = +1 \middle| \sum_i e_i r_i^2 \cdot \sin^2\theta_{iz} \cdot e^{i2\phi}) \middle| \Lambda = -1 >_{CD} \right\rangle \tag{10}$$

The nuclear contribution is $\langle zz\rangle_{nuc} = Z_X r_X^2 + Z_Y r_Y^2$, with r_X and r_Y being the atomic coordinates in the chosen origin. The latter corresponds to the center of mass for most of the present diatomics, except for the excited states A$^3\Pi$ (NH) and A$^2\Sigma^+$ (OH), for which the center of positive charge is used (GO3 calculations collapse into the ground state when skipping the standard orientation).

Table 4 lists the calculated Θ's for all Π species, together with those for a low-lying Σ state. Relevant quantities are $\Theta_{zz} = z^2 - (x^2 + y^2)/2$ and $\delta\Theta_\Pi = \lvert\Theta_{xx} - \Theta_{yy}\rvert = (3/2)\lvert x^2 - y^2\rvert$. Other parameters in Table 4 are the electric dipole moment (μ), Cartesian second moments, and the spatial extent $\langle r^2\rangle_{el}$.

Since Π states have $\delta\Theta_\Pi \neq 0$, their CDD contours *in the xy-plane* are elliptically shaped (vs circularly shaped in Σ states). No experimental Θ's are known for any of these radicals, except NO (Table 4). To the best of our knowledge, theoretical Θ's are available for three cases (CH, OH, NO), but only OH was correctly described via its complete set $\{\Theta_{zz}, \delta\Theta_\perp\}$ (Table 4).

Regarding the terms involved in $\Theta_{zz} = [z^2 - (x^2 + y^2)/2]$, all electronic second moments are intrinsically *negative* ($x^2_{el} < 0$, etc.), whereas the *positive* nuclear contribution z^2_{nuc} only affects z^2. Therefore, for neutral XY one expects $\lvert z^2\rvert_{el} > \lvert z^2\rvert_{nuc}$. More precisely, a negative Θ_{zz} describes a "prolate" CDD since $\lvert z^2\rvert$ is larger than the average $\lvert x^2 + y^2\rvert/2$, as found, for example, in O_2, NO, N_2, CO, and CO_2. Complementarily, $\Theta_{zz} > 0$ reveals an "oblate" CDD, as in FH, ClH, CS_2, and C_2H_2.[5g,19,28]

Our calculations find Θ_{zz} to be negative for X$^2\Pi$ radicals with one unpaired π-electron, like ($\sigma^2\pi$) in CH, or ($\sigma^2\pi^4\pi$) in NO, CF. Conversely, $\Theta_{zz} > 0$ for $^2\Pi(\pi^3)$ radicals like OH, LiO, and FO.

As said before, a Π and a Σ state each have been considered for all radicals in Table 4. From CH to CF, the corresponding excited state arises via an excitation $\sigma \rightarrow \pi(\pi^*)$ relative to the ground state. Upon excitation, Θ_{zz} always increases. The $^4\Sigma^-$ state of FO arises from a $\pi^* \rightarrow \sigma^*$ excitation relative to X$^2\Pi(\pi^4\pi^{*3})$, resulting in a decrease in Θ_{zz} (both values are positive and small, Table 4).

Rodrigues and Varandas[29] calculated for CH (X$^2\Pi$, a$^4\Sigma^-$), NH (X$^3\Sigma^-$), and OH (X$^2\Pi$) the function $\Theta_{zz}(R)$. The values in Figures 1−4 from ref 29 are in line with our data in Table 4. However, their discussion about atom−diatom electrostatic interactions between the three diatomics above should be revised since X$^2\Pi$ states were assumed to have axially symmetric CDDs.

Experimental Θ's are only available for NO.[3,5g,28] Tejwani et al.[10c] found Θ′(NO) = 1.78 au, supporting a median ⟨Θ′⟩ = 1.58 au from other (eight) experimental values from 1.4 to 2.3 au (sign unknown). Since those works reported Θ′ = 2Θ (section III.A), the corrected values are Θ = 0.89 and ⟨Θ⟩ = 0.79 au. Our calculations and two others[5e,f] agree with experiments, but Θ_{zz}(NO) is negative (−0.83 to −0.88 au); less

TABLE 4: Parallel (Θ_{zz}) and Perpendicular ($\delta\Theta_\Pi$) Components of the Molecular Quadrupole Moment[a]

XY	state	ref	μ[b]	Θ_{zz}[c]	$\delta\Theta_\Pi$[d]	$-\langle z^2\rangle$[e]	$-\langle x^2, y^2\rangle$[f]	$\langle r^2\rangle_{el}$[g]
CH	$X^2\Pi(\sigma^2\pi)$	tw	0.57	−0.55	1.35	$\underline{5.63}$	$\underline{5.08}$	19.78
		9a	0.57	−0.69	(0)			
	$a^4\Sigma^-(\sigma\pi^2)$	tw	0.26	1.59	0	4.03	5.62	18.94
		9a	0.26	2.08				
NH	$X^3\Sigma^-(\sigma^2\pi^2)$	tw	0.60	0.47	0	4.33	4.80	17.38
	$A^3\Pi\ (\sigma\pi^3)$[h]	tw	0.50	2.45	2.17	3.15	5.60	17.72
OH	$X^2\Pi(\sigma^2\pi^3)$	tw	0.65	1.12	1.47	3.53	4.65	15.82
		6d, e		1.35	1.31[i]			
		6k	0.65	1.39	1.18			
		6g	0.64	1.39	(0)			
	$A^2\Sigma^+(\sigma\pi^4)$	tw	0.71	3.00	0	2.35	5.28	16.17
		6g	0.72	3.18	0			
LiO	$X^2\Pi(\sigma^2\pi^3)$	tw	−2.56	4.13	1.82	1.99	6.12	36.55
	$A^2\Sigma^+(\sigma\pi^4)$	tw	−2.25	5.38	0	1.30	6.68	33.90
NO	$X^2\Pi(\sigma^2\pi^4\pi^*)$	tw	0.05	−0.88	0.86	$\underline{8.54}$	$\underline{7.66}$	41.51
	expt	10c	0.06[j]	0.89				
		5e	0.06	−0.83	(0)			
		5f	0.07	−0.83	(0)			
		5a	0.10	−0.68	(0)			
		5b	0.06	−0.72	(0)			
	$^4\Sigma^-(\sigma\pi^4\pi^{*2})$	tw	−0.29	1.14	0	7.03	8.17	46.53
CF	$X^2\Pi(\sigma^2\pi^4\pi^*)$	tw	0.31	−1.33	0.14	$\underline{9.25}$	$\underline{7.92}$	45.73
	$^4\Sigma^-(\sigma\pi^4\pi^{*2})$	tw	−0.24	0.69	0	7.45	8.14	46.40
FO	$X^2\Pi(\pi^4\pi^{*3})$	tw	-0.00_4	0.19	1.08	7.26	7.45	49.92
		14a	−0.14	0.10				
	$^4\Sigma^-(\pi^4\pi^{*2}\sigma^*)$	tw	−0.69	−0.40	0	$\underline{7.75}$	$\underline{7.35}$	72.49

[a] Dipole moments (μ), second moments, and electronic spatial extent are also given. All data in atomic units. [b] Expectation value $\langle z\rangle$. A positive μ indicates a X^-Y^+ polarity. [c] $\Theta_{zz} = z^2 - (x^2 + y^2)/2$. In general, $\Theta_{ii} = \langle ii\rangle - (\langle jj) + \langle kk\rangle)/2$, with $\{ii, jj, kk\} \equiv \{xx, yy, zz\}$. Unless specified otherwise (footnote[h]), origin at center of mass for each of the most abundant isotope. [d] $\delta\Theta_\Pi = |\Theta_{xx} - \Theta_{yy}| = (3/2)|x^2 - y^2|$. [e] $z^2 = z^2_{el} + z^2_{nuc}$, where z^2_{el} and z^2_{nuc} are negative and positive, respectively. For illustration, Cartesian second moments are underlined when $\Theta_{zz} < 0$. [f] $-\langle x^2, y^2\rangle$ stands for the average $-(x^2 + y^2)/2$. Note that $x^2 \equiv x^2_{el}$ and $y^2 \equiv y^2_{el}$. [g] $\langle r^2\rangle_{el} = -\sum\langle ii\rangle_{el}$. [h] Origin at center of positive charges (see text). [i] Original value of 2.62 au for $\delta\Theta'_\Pi = |\Theta'_{xx} - \Theta'_{yy}| = 3|x^2 - y^2|$, i.e., Hirschfelder et al. quadrupole (ref 16). [j] Ref 10a.

extensive studies found −0.68[5a] and −0.72 au.[5b] All previous studies neglected $\delta\Theta_\Pi$, which according to our results $\{\Theta_{zz}, \Theta_{xx}, \Theta_{yy}\} = \{-0.88, 0.87, 0.01$ au$\}$ corresponds to $\delta\Theta_\Pi = 0.86$ au. (Assumption of axial symmetry gives $\{-0.88, 0.44, 0.44$ au$\}$ instead.) Theoretical studies[5f,g] dealing with the second-virial/dispersion coefficients and anisotropic dipole properties of NO should be taken with caution since they assumed $\delta\Theta_\Pi = 0$.

IV. Discussion

The results in Tables 1−4 confirm that a correct description of *traceless* second-rank tensor properties in Π states requires *two* independent parameters, the parallel ($P_\|$) and perpendicular ($\delta P_\perp$) anisotropies. These statements are in line with experimental studies on the magnetic (T_{ii}) and electric (q_{ii}) hyperfine cc's of Π states. From the very beginning (1950s), spectroscopists took properly into account the axial asymmetry of the CDD/SDDs for $|\Lambda| = 1$ states,[1,2] by providing two independent parameters each, $\{c, d\}$ and $\{q_0, q_2\}$. The situation is different for molecular Θ's since they are not only difficult to measure experimentally[3,28] but available data are mostly rotational averages ($\delta\Theta_\perp$ cannot be detected). However, there is no doubt that Π states also have two independent Θ's since (1) all hfcc's indicate the CDD/SDDs to be axially *asymmetric* around each nucleus, and the same should apply to the whole molecule,[4] (2) the T_{ii}, q_{ii}, and Θ_{ii} operators share the same rotational symmetry properties,[30] and (3) as shown next, two other experimental processes—collisions X_2 + M, and van der Waals (vdW) interactions—provide support to our statements.

Scattering studies in the 1970s involving $A^1\Pi_u$ of Na_2 and Li_2 found the rainbow spectra to be markedly different from those with $X^1\Sigma_g^+$ states.[31] Prior interpretations had assumed the multipole expansion $V(r, \theta) = \sum_l V_l(r)P^l(\cos\theta)$ of the X_2-potential to be valid for *any* Λ-value. However, the $A^1\Pi_u$ spectra could not be reproduced by a cylindrically symmetric potential $V(r, \theta)$ with only one anisotropy (Θ_{zz}). The discrepancy was lifted[32] using the multipole expansion

$$V(r, \theta, \phi) = V_{00}(r) + V_{20}(r)L_0^{\ 2}(\cos\theta) + (4\pi/5)^{1/2}V_{22}(r)[Y_2^{(2)}(\theta, \phi) + Y_{-2}^{(2)}(\theta, \phi)] + \ldots, \quad (11)$$

including the extra term $Y_{\pm2}{}^2(\theta, \varphi)$ to describe axial asymmetry. Now, up to the quadrupole, the Π potential $V(r, \theta, \varphi)$ contains three terms: (1) $V_{00}(r)$, the isotropic term equivalent to $P_0^{\ 0}$ [$\propto r^2$], (2) one parallel anisotropy $L_0^{\ 2}(\cos\theta)$ [equivalent to $P_0^{\ 2} = \Theta_{zz} = (z^2 - (x^2 + y^2)/2)$], and (3) a perpendicular anisotropy $(Y_2^{(2)}(\theta, \varphi) + Y_{-2}^{(2)}(\theta, \varphi))$ [equivalent to $P_{|2|}{}^2 = \delta\Theta_\perp = |\Theta_{xx} - \Theta_{yy}| = (3/2)|x^2 - y^2|$].

The interesting question now arises about the behavior expected for X_2 + M collisions involving a $^{2S+1}\Delta_{(g,u)}$ state [$\Lambda = 2$], like the long-lived $a^1\Delta_g(O_2)$ state. We are unaware of experimental studies of XY(Δ) + M(^{1}S) collisions. As previously discussed,[4] the CDD/SDDs of Δ states behave as axially *symmetric* for 2^l-poles with $l = 1, 2, 3$, but *asymmetric* for $l \geq 4$. The multipole expansion (up to the hexadecapole and omitting r dependency) reads as

$$V(\theta, \phi) = V_{00} + V_{20}L_0^{\ 2}(\cos\theta) + V_{40}L_0^{\ 4}(\cos\theta) + kV_{44}[Y_4^{(4)}(\theta, \phi) + Y_{-4}^{(4)}(\theta, \phi)] + \ldots, \quad (12)$$

The first two terms are the isotropic and *parallel* quadrupolar contributions, whereas the last three are the hexadecapole anisotropies, one parallel [$L_0^{\ 4}(\cos\theta)$] and one perpendicular [$Y_4^{(4)} + Y_{-4}^{(4)}$].

TABLE 5: Comparison between Different Magnetic (*T*) and Electric (*q*) Coupling Constants[a]

	$-(2/3)T_{zz}$ $(-c)$	q_{zz} $(-q_0)$	$\|T_{xx} - T_{yy}\|$ $(\|d\|)$	$\|q_{xx} - q_{yy}\|$ $(\|q_2\|/2)$	$\delta(T/q)_\perp$[b]	$-d/c$
$\underline{C}H$ (π^1)	1.017	1.027	2.104	2.024	1.04	2.07
$\underline{C}F$ (π^1)	1.114	0.233	2.163	2.019	1.07	1.94
$\underline{N}O$ (π^1)	1.531	0.478	2.992	2.703	1.11	1.95
$N\underline{O}$ (π^1)	1.319	−0.205	2.897	2.896	1.00	2.20
$\underline{O}H$ (π^3)	2.977	−0.281	5.992	5.146	1.16	2.01
$Li\underline{O}$ (π^3)	2.772	1.632	5.346	4.304	1.24	1.93
$F\underline{O}$ (π^3)	2.881	−3.245	5.851	5.129	1.14	2.03
$C\underline{F}$ (π^1)	0.703	−1.554	1.639	1.849	0.89	2.33
$\underline{F}O$ (π^3)	1.244	−4.393	2.158	1.983	1.09	1.73

[a] All data in atomic units. [b] $\delta(T/q)_\perp = [\delta T_\perp/\delta q_\perp\ ] = |T_{xx} - T_{yy}|/|q_{xx} - q_{yy}| = 2|d/q_2|$.

Also interesting is the 1976 paper by Nielson et al.[10b] about vdW interactions of diatomic Π states with atoms, in particular the C_6 coefficient for NO($X^2\Pi$) plus noble-gas M(^1S). Independent of the developments on collision theory discussed above, these authors found that a correct description of the NO potential requires the inclusion of $Y_m^{(l)}(\theta, \varphi)$ with $m = 0, \pm 2$ for $l = 2$. Nielson et al. also mentioned that theoretical C_6 coefficients for $\Delta(\Lambda = 2)$ and $\Phi(\Lambda = 3)$ states have to include $Y_{0,\pm 4}^{(l \geq 4)}(\theta, \varphi)$ and $Y_{0,\pm 6}^{(l \geq 6)}(\theta, \varphi)$, respectively, as independently shown by us for multipoles.[4]

One important difference between $^2\Sigma^+$ and $^2\Pi$ states, at least from the standpoint of the hfcc's, is that the perpendicular parameters d and q_2 carry the most relevant information about the $^2\Pi$ state (they are also related to the atomic values),[33] whereas the corresponding parallel terms c and q_0 are seldom discussed by experimentalists. The opposite picture holds for $^2\Sigma^+$ states, where (let us say, by symmetry restraints) the only parameters are c and q_0. For example, for N_2^+ we have calculated $c = 84$ MHz for $X^2\Sigma_g^+$, to be compared with $d = 77$ MHz in the $A^2\Pi_u$ state.[30]

Other relations between hfcc's could be of general interest. Table 5 compares theoretical values for tensor components of the same kind, i.e., parallel (c vs q_0) and perpendicular (d vs $q_2/2$). This table also lists two relevant ratios, one between perpendicular anisotropies ($\delta T_\perp/\delta q_\perp$) and the other between magnetic hfcc's ($-d/c$). As seen in Table 5, no correlation is apparent between c and q_0, neither on signs nor magnitudes. Since the efg parameter q_0 contains a nuclear contribution from the neighboring atomic center, one may think that correcting q_0 to get the pure electronic contribution (as in c) could solve the problem, but this is not the case (charge transfer along z might significantly alter the CDD expected for corresponding p_z-orbitals).

On the other hand, a very nice correlation exists between the perpendicular magnetic and electric components, with the ratio $\delta T_\perp/\delta q_\perp = |T_{xx} - T_{yy}|/|q_{xx} - q_{yy}|$ generally lying slightly above 1.0 (only CF has a low ratio of 0.89). Thus, contour lines in the xy-plane are quite similar for both CDDs and SDDs. Also, experimental and theoretical atomic data[1,24] indicate that $\langle 1/r^3\rangle_{SDD}$ is about 10% larger than $\langle 1/r^3\rangle_{CDD}$, and the same trend is found here for the present radicals.

The ratio $-d/c$ lies close to 2. According to the literature,[1,24] for a p_π-electron the expectation value $\mathbf{I} = \langle p_\pi|(3\cos^2\theta - 1)|p_\pi\rangle = -2/5$, whereas that of $\mathbf{II} = \langle p_\pi|(3\sin^2\theta)|p_\pi\rangle = 4/5$. Since c and d are, respectively, proportional to **I** and **II**, pure p_π-AOs in isolated atoms should have a ratio $-d/c = 2$. As seen in Table 5, the diatomics studied here deviate little from the atomic cases. Note that the F atom in both CF and FO appears to the most distorted among all systems considered.

V. Concluding Remarks

Here, attention has been called to a common error in the literature:[3,34,35] that charge- and spin-DDs are axially symmetric in *any* linear state (i.e., $x^2 = y^2 \neq z^2$ or $P_{xx} = P_{yy} = -P_{zz}/2$ for traceless P_{ii}). Our calculations successfully describe the axial asymmetry of the CDD/SDDs in $X^2\Pi$ states [ref 18, p 367]. Two different molecular regions have been investigated: (1) those close to the nuclei (magnetic/electric hfcc's proportional to $\langle 1/r^3\rangle$) and (2) those toward the outermost regions (Cartesian second-moments $\langle ii\rangle^2$ or their linear combinations Θ_{ii}). The three traceless properties have been calculated with the B3LYP/aug-cc-pVQZ method for all neutral $X^2\Pi$ ground states containing H to F atoms. The calculated values reproduce well experimental and more sophisticated theoretical data. Except for OH, our $\{\Theta_{zz}, \delta\Theta_\perp\}$'s are new for all diatomics considered here.

The traceless tensors $P_{ii} = T_{ii}$, q_{ii}, Θ_{ii} exhibit the same properties upon (the symmetry operation of) rotation about the molecular axis z.[36] Thus, regarding the number of independent terms, all three tensors share a common behavior (spin multiplicity is irrelevant): Π states have $n = 2$ independent components (anisotropies),[4] whereas all other (non-Π) states have $n = 1$. These constraints are well-known to experimental spectroscopists, who always report the pairs (c,d) and (q_0, q_2) for a given Π state, but just c and q_0 for all other electronic states (Σ, Δ, Φ, etc.). No direct experimental determinations of Θ_{zz} and $\delta\Theta_\perp$ are available to verify that Π states also have two independent anisotropies. However, the rainbow spectra of $X_2(\Pi) + M(S)$ collisions could only be interpreted by including *two independent* quadrupole terms in the multipole expansion of the Π potential. Gratefully, this corroborates the existence of two independent quadrupoles predicted by theory.

Certainly, the axial asymmetry of the CDD/SDDs in linear Π states affects all properties depending on these density distributions. This applies, besides the traceless properties studied here, to traced tensors as well—for example, dipole (hyper)polarizabilities α and β,[37] magnetizabilities, and NMR chemical shifts[26]—which should have $n = 3$ independent parameters for Π states (isotropic term plus two anisotropies). For the same properties, Σ states have $n = 2$ (i.e., just one anisotropy).

Acknowledgment. The authors thank NSERC (Canada) for financial support.

References and Notes

(1) (a) Frosch, R. A.; Foley, H. M. *J. Chem. Phys.* **1952**, *88*, 1337. (b) Weltner, W. *Magnetic Atoms and Molecules*; Dover: New York, 1983. (c) Hirota, E. *High-Resolution Spectroscopy of Transient Molecules*; Springer: Berlin, 1985.

(2) Das, T. P.; Hahn, E. L. *Solid State Phys., Suppl.* **1958**, *1*, 1.

(3) Buckingham, A. D. *Q. Rev. Chem. Soc.* 1959, *13*, 183; *J. Chem. Phys.* 1959, *30*, 1580; *Adv. Chem. Phys.* 1967, *12*, 107; in *Physical*

Chemistry. An Advanced Treatise; Henderson, D., Ed.; Academic Press: New York, 1970; Vol. IV, Molecular Properties, p 349.

(4) Bruna, P. J.; Grein, F. *J. Chem. Phys.* **2007**, *127*, 074107.

(5) (a) Green, S. *Chem. Phys. Lett.* **1972**, *13*, 552; **1973**, *23*, 115. (b) Billingsley, F. P. *J. Chem. Phys.* **1975**, *62*, 864. (c) Walch, S. P.; Goddard, A. *Chem. Phys. Lett.* **1975**, *33*, 18. (d) Cummins, P. L.; Bacskay, G. B.; Hush, N. S.; Ahlrichs, R. *J. Chem. Phys.* **1987**, *86*, 6908. (e) Feller, D.; Glendening, E. D.; Cullough, E. A.; Miller, R. J. *J. Chem. Phys.* **1993**, *99*, 2829. (f) Meng, L.; Duan, Y.-Y. *Mol. Phys.* **2006**, *104*, 2891. (g) Buendgen, P.; Grein, F.; Thakkar, A. J. *J. Mol. Struct. (THEOCHEM)* **1995**, *334*, 7. (h) Buendgen, P.; Thakkar, A. J.; Kumar, A.; Meath, W. J. *Mol. Phys.* **1997**, *90*, 721. (i) Polak, R.; Fiser, J. *Chem. Phys.* **2004**, *303*, 73; **2006** *326*, 611; **2008**, *351*, 83.

(6) (a) Radford, H. E. *Phys. Rev.* **1961**, *122*, 114; **1962**, *126*, 1035. (b) Kayama, K. *J. Chem. Phys.* **1963**, *39*, 1507. (c) Bender, C. F.; Davidson, E. R. *Phys. Rev.* **1969**, *183*, 23. (d) Chu, S. I.; Yoshimine, M.; Liu, B. *J. Chem. Phys.* **1974**, *61*, 5389. (e) Chu, S. I. *Astrophys. J.* **1976**, *206*, 640. (f) Coxon, J. A.; Sastry, K. V.; Austin, J. A.; Levy, D. H. *Can. J. Phys.* **1979**, *57*, 619. (g) Degli Esposti, A. D.; Werner, H.-J. *J. Chem. Phys.* **1990**, *93*, 3351. (h) Graff, M. M.; Wagner, A. F. *J. Chem. Phys.* **1990**, *92*, 2423. (i) Chong, D.; Langhoff, S. R.; Bauschlicher, C. W. *J. Chem. Phys.* **1991**, *94*, 3700. (j) Bailey, W. C. *Chem. Phys. Lett.* **1998**, *292*, 71. (k) Wormer, P. E. S.; Klos, J. A.; Groenenboom, G. C.; van der Avoird, A. *J. Chem. Phys.* **2005**, *122*, 244325. (l) Fitzpatrick, J. A.; Manby, F. R.; Western, C. M. *J. Chem. Phys.* **2005**, *122*, 084312. (m) Spelsberg, D. *J. Chem. Phys.* **1999**, *111*, 9625. (n) Bussery-Honvault, B.; Dayou, F.; Zanchet, A. *J. Chem. Phys.* **2008**, *129*, 234302.

(7) Ubachs, W.; Ter Meulen, J. J.; Dymanus, A. *Can. J. Phys.* **1984**, *62*, 1374.

(8) Gammon, R. H.; Stern, R. C.; Lesk, M. E.; Wicke, B. G.; Klemperer, W. *J. Chem. Phys.* **1971**, *54*, 2136.

(9) (a) Lie, G.; Hinze, J.; Liu, B. *J. Chem. Phys.* **1973**, *59*, 1887. (b) Kristiansen, P.; Veseth, L. *J. Chem. Phys.* **1986**, *84*, 2711, 6336. (c) Engels, B.; Peyerimhoff, S. D.; Karna, S. P.; Grein, F. *Chem. Phys. Lett.* **1988**, *152*, 397. (d) Momose, T.; Yamaguchi, M.; Shida, T. *J. Chem. Phys.* **1990**, *93*, 7285. (e) Davidson, S. A.; Evenson, K. M.; Brown, J. M. *J. Mol. Spectrosc.* **2004**, *223*, 20.

(10) (a) Neumann, R. M. *Astrophys. J.* **1970**, *161*, 779. (b) Nielson, G. C.; Parker, G. A.; Pack, R. T. *J. Chem. Phys.* **1976**, *64*, 2055. (c) Tejwani, G. D. T.; Golden, B. M.; Yeung, E. S. *J. Chem. Phys.* **1976**, *65*, 5110. (d) Western, C. M.; Langridge-Smith, P. R. R.; Howard, B. J.; Novick, S. E. *Mol. Phys.* **1981**, *44*, 145. (e) Saleck, A. H.; Yamada, K. M. T.; Winnewisser, G. *Mol. Phys.* **1991**, *72*, 1135. (f) Saleck, A. H.; Liedtke, M.; Dolgner, A.; Winnewisser, G. *Z. Naturforsch.* **1994**, *A49*, 1111. (g) Klisch, E.; Belov, S. P.; Schieder, R.; Winnewisser, G.; Herbst, E. *Mol. Phys.* **1999**, *97*, 65.

(11) (a) Carrington, A.; Lucas, N. J. D. *Proc. R. Soc. London, Ser. A* **1970**, *314*, 567. (b) Gwinn, W. D.; Turner, B. E.; Gross, W. M.; Blackman, G. L. *Astrophys. J.* **1973**, *179*, 789. (c) Steimle, C.; Woodwrad, D. R.; Brown, J. M. *J. Chem. Phys.* **1986**, *85*, 1296. (d) Leopold, K. R.; Evenson, K. M.; Comben, E. R.; Brown, J. M. *J. Mol. Spectrosc.* **1987**, *122*, 440.

(12) (a) Feund, S. M.; Herbst, E.; Mariella, R. P.; Klemperer, W. *J. Chem. Phys.* **1972**, *56*, 1467. (b) Yamada, C.; Fujitake, M.; Hirota, E. *J. Chem. Phys.* **1989**, *91*, 137.

(13) (a) Hall, J. A.; Richards, W. G. *Mol. Phys.* **1972**, *23*, 331. (b) Brown, J. M.; Schubert, J. E.; Saykally, R. J.; Evenson, K. M. *J. Mol. Spectrosc.* **1986**, *120*, 421. (c) Morino, I.; Yamada, K. M.; Belov, S. P.; Winnewisser, G.; Herbst, E. *Astrophys. J.* **2000**, *532*, 377.

(14) (a) O'Hare, P. A. G.; Wahl, A. C. *J. Chem. Phys.* **1970**, *53*, 2469. (b) Tomassia, F.; Brown, J. M.; Evenson, K. M. *J. Chem. Phys.* **1999**, *110*, 7273. (c) Tomassia, F.; Brown, J. M.; Saito, S. *J. Chem. Phys.* **2000**, *112*, 5523. (d) Tomassia, F.; Brown, J. M.; Watson, J. K. G. *Mol. Phys.* **2002**, *100*, 3485.

(15) (a) Fano, U.; Racah, G. *Irreducible Tensorial Sets*; Academic Press: New York, 1959. (b) Silver, B. L. *Irreducible Tensor Methods*; Academic Press: New York, 1976.

(16) Hirschfelder, J. O.; Curtiss, C. F.; Bird, R. B. *Molecular Theory of Gases and Liquids*; J. Wiley & Sons: New York, 1954.

(17) McLean, A. D.; Yoshimine, M. *J. Chem. Phys.* **1967**, *47*, 1927.

(18) Brown, J. M.; Carrington, A. *Rotational Spectroscopy of Diatomic Molecules*; Cambridge University Press: Cambridge, U.K., 2003.

(19) (a) Lawson, D. B.; Harrison, J. F. *J. Phys. Chem. A* **1997**, *101*, 4781; *Mol. Phys.* **1998**, *93*, 519. (b) Harrison, J. F. *J. Chem. Phys.* **2003**, *119*, 8763; **2008**, *128*, 114320.

(20) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J. J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. Gaussian 03, revision B.04; Gaussian, Inc.: Pittsburgh, PA, 2003.

(21) Huber, K. P.; Herzberg, G. *Molecular Spectra and Molecular Structure*; Van Nostrand-Reinhold: New York, 1979; Vol. IV.

(22) Engels, B.; Eriksson, L. A.; Lunell, S. *Adv. Quantum Chem.* **1996**, *27*, 298.

(23) Geisen, H.; Neuschaefer, D.; Ottinger, Ch. *Z. Phys. D: At., Mol. Clusters* **1990**, *17*, 137.

(24) Hirota, E. *J. Phys. Chem.* **1983**, *87*, 3375.

(25) Rajendra, Pd.; Chandra, P. *J. Chem. Phys.* **2001**, *114*, 1589.

(26) Flygare, W. H. *Molecular Structure and Dynamics*; Prentice-Hall: Englewood Cliffs, NJ, 1978.

(27) (a) Sugimoro, K.; Mizobuchi, A.; Nakai, K. *Phys. Rev.* **1964**, *134*, B539. (b) Kreische, W.; Maar, H. U.; Niedrig, H.; Reuter, K.; Roth, K. *Hyperfine Interact.* **1978**, *4*, 732. (c) Mishra, K. C.; Duff, K. J.; Das, T. P. *Phys. Rev. B* **1982**, *25*, 3389. (d) Barfuss, H.; Boehnlein, G.; Gradl, G.; Hohenstein, H.; Kreische, W.; Niedrig, H.; Reimer, A. *J. Chem. Phys.* **1982**, *76*, 5103. (e) Tossell, J. A.; Lazzeretti, P. *J. Phys. B: At. Mol. Opt. Phys.* **1986**, *19*, 3217. (f) Bertholdt, E.; Frank, M.; Gubitz, F.; Kreische, W.; Loesch, B.; Ott, Ch.; Roeseler, B.; Schneider, M.; Schwab, F.; Stammler, K.; Weeske, G. *J. Mol. Struct.* **1989**, *192*, 383. (g) Pyykko, P. *Mol. Phys.* **2008**, *106*, 1965.

(28) (a) Stogryn, D. E.; Stogryn, A. P. *Mol. Phys.* **1966**, *11*, 371. (b) Krishnaji, V. P. *Rev. Mod. Phys.* **1966**, *38*, 690.

(29) Rodrigues, S. P. J.; Varandas, A. J. C. *Phys. Chem. Chem. Phys.* **2000**, *2*, 435.

(30) Bruna, P. J.; Grein, F. *J. Mol. Spectrosc.* **2008**, *250*, 75.

(31) (a) Ottinger, Ch.; Velasco, R.; Zare, R. N. *J. Chem. Phys.* **1970**, *52*, 1636. (b) Ottinger, Ch.; Poppe, D. *Chem. Phys. Lett.* **1971**, *8*, 513. (c) Bergmann, K.; Demtroeder, W. *J. Phys. B: At. Mol. Opt. Phys.* **1972**, *5*, 1386, 2098.

(32) Klar, H. *J. Phys. B: At. Mol. Opt. Phys.* **1973**, *6*, 2139.

(33) Bruna, P. J.; Grein, F. *Mol. Phys.* **2006**, *104*, 429.

(34) (a) Jansen, L. *Physica* **1957**, *23*, 599; *Phys. Rev.* **1958**, *110*, 661. (b) Kielich, S. *Physica* **1965**, *31*, 444.

(35) (a) Buckingham, A. D.; Pople, J. A. *Proc. Phys. Soc. London* **1955**, *A68*, 905. (b) Buckingham, A. D.; Stephen, M. J. *Trans. Faraday Soc.* **1957**, *53*, 884.

(36) Hougen, J. In *Physical Chemistry. An Advanced Treatise*; Henderson, D., Ed.; Academic Press: New York, 1970; Vol. IV, Molecular Properties, p 390.

(37) *Atoms, Molecules and Clusters in Electric Fields: Theoretical Approaches to the Calculationof Electric Polarizability*; Maroulis, G., Ed.; Imperial College Press: London, 2006.

JP807885C