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# Quadrupole, octopole, and hexadecapole electric moments of $\Sigma$ , $\Pi$ , $\Delta$ , and $\Phi$ electronic states: Cylindrically asymmetric charge density distributions in linear molecules with nonzero electronic angular momentum

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The number of independent components,  $n$ , of traceless electric  $2^l$ -multipole moments is determined for  $C_{\infty v}$  molecules in  $\Sigma^\pm$ ,  $\Pi$ ,  $\Delta$ , and  $\Phi$  electronic states ( $\Lambda=0, 1, 2, 3$ ). Each  $2^l$  pole is defined by a rank- $l$  irreducible tensor with  $(2l+1)$  components  $P_m^{(l)}$  proportional to the solid spherical harmonic  $r^l Y_m^l(\theta, \varphi)$ . Here we focus our attention on  $2^l$  poles with  $l=2, 3, 4$  (quadrupole  $\Theta$ , octopole  $\Omega$ , and hexadecapole  $\Phi$ ). An important conclusion of this study is that  $n$  can be 1 or 2 depending on both the multipole rank  $l$  and state quantum number  $\Lambda$ . For  $\Sigma^\pm(\Lambda=0)$  states, all  $2^l$  poles have one independent parameter ( $n=1$ ). For spatially degenerate states— $\Pi$ ,  $\Delta$ , and  $\Phi$  ( $\Lambda=1, 2, 3$ )—the general rule reads  $n=1$  for  $l < 2|\Lambda|$  (when the  $2^l$ -pole rank lies below  $2|\Lambda|$ ) but  $n=2$  for higher  $2^l$  poles with  $l \geq 2|\Lambda|$ . The second nonzero term is the off-diagonal matrix element  $\langle \psi_{+\Lambda} | P_{|m|=2\Lambda}^{(l)} | \psi_{-\Lambda} \rangle$ . Thus, a  $\Pi(\Lambda=1)$  state has *one* dipole ( $\mu_z$ ) but *two* independent  $2^l$  poles for  $l \geq 2$ —starting with the quadrupole  $[\Theta_{zz}, (\Theta_{xx} - \Theta_{yy})]$ . A  $\Delta(\Lambda=2)$  state has  $n=1$  for  $2^{(1,2,3)}$  poles ( $\mu_z, \Theta_{zz}, \Omega_{zzz}$ ) but  $n=2$  for higher  $2^{(l \geq 4)}$  poles—from the hexadecapole  $\Phi$  up. For  $\Phi(\Lambda=3)$  states, it holds that  $n=1$  for  $2^1$  to  $2^5$  poles but  $n=2$  for all  $2^{(l \geq 6)}$  poles. In short, what is usually stated in the literature—that  $n=1$  for all possible  $2^l$  poles of linear molecules—only applies to  $\Sigma^\pm$  states. For degenerate states with  $n=2$ , all Cartesian  $2^l$ -pole components ( $l \geq 2|\Lambda|$ ) can be expressed as linear combinations of two irreducible multipoles,  $P_{m=0}^{(l)}$  and  $P_{|m|=2\Lambda}^{(l)}$  [parallel ( $z$  axis) and anisotropy ( $xy$  plane)]. Our predictions are exemplified by the  $\Theta$ ,  $\Omega$ , and  $\Phi$  moments calculated for  $\Lambda=0-3$  states of selected diatomics (in parentheses):  $X^2\Sigma^+(\text{CN})$ ,  $X^2\Pi(\text{NO})$ ,  $a^3\Pi_u(\text{C}_2)$ ,  $X^2\Delta(\text{NiH})$ ,  $X^3\Delta(\text{TiO})$ ,  $X^3\Phi(\text{CoF})$ , and  $X^4\Phi(\text{TiF})$ . States of  $\Pi$  symmetry are most affected by the deviation from axial symmetry. © 2007 American Institute of Physics. [DOI: 10.1063/1.2755691]

## I. INTRODUCTION

This work investigates the properties related to the rotational symmetry—with respect to (the symmetry operation of) rotation around the molecule-fixed  $z$  axis—of the charge density distribution (CDD) of linear molecules in spatially degenerate states, i.e., those where the projection  $\Lambda$  along  $z$  of the total electronic angular momentum (excluding spin) is nonzero ( $\Lambda=1, 2, 3, 4$  for  $\Pi$ ,  $\Delta$ ,  $\Phi$ ,  $\Gamma$ ).<sup>1,2</sup> The CDD will be represented by traceless  $2^l$ -pole moments,<sup>3-6</sup> with the corresponding number of independent components given by the parameter  $n$ .

Any linear state is described by a wave function  $\Psi_\Lambda$  proportional to  $e^{i\Lambda\varphi} = (\cos \Lambda\varphi + i \sin \Lambda\varphi)$ , where  $\varphi$  is the azimuthal angle around  $z$ . The CDD  $\propto (\Psi_\Sigma^* \Psi_\Sigma)$  is  $\varphi$  independent for a  $\Sigma^{(\pm)}(\Lambda=0)$  state only, i.e., it remains constant along any circle of radius  $r_z$  perpendicular to the  $z$  axis. A  $\Sigma$ -type CDD is referred to as being cylindrically, or axially, symmetric upon  $z$  rotation. Thus, a  $\Sigma$ -type CDD is such that  $n=1$  for every multipole moment. By the same token, CDD's of degenerate states ( $\Lambda \neq 0$ )—due to their  $\varphi$  dependency—cannot

be cylindrically symmetric, i.e., degenerate states should have a larger  $n$  value. In spite of such a clear distinction between  $\Lambda=0(\Sigma)$  and  $\Lambda=1(\Pi)$ , there exist in the literature conflicting statements about how many independent terms are needed in  $\Pi$  states to describe the electric field gradient ( $q_{ij}$ ) and quadrupole moment ( $\Theta_{ij}$ ).<sup>1,2</sup> For  $\text{NO}(X^2\Pi)$ , experimental studies<sup>1,2</sup> find, correctly, that there are *two* independent  $q$  values [ $q_{zz} \propto (3 \cos^2 \theta - 1)$  and  $(q_{xx} - q_{yy}) \propto (\sin^2 \theta)$ ] whereas theoretical calculations<sup>7,8</sup> state that *one* component [ $\Theta_{zz} \propto (3 \cos^2 \theta - 1)$ ] suffices to characterize the quadrupole. Calculated  $\Theta$  moments for  $1^2\Pi$  of OH,  $\text{CO}^+$ , and  $\text{N}_2^+$  have also assumed  $n=1$ .<sup>9-11</sup>

One of our goals is to clarify, for the electric  $2^l$ -pole moments in linear molecules ( $C_{\infty v}$ ), the dependency of  $n$  on the  $\Lambda$  value. The rotational-symmetry properties of states with  $\Lambda=0-3$  will be analyzed by considering three electric  $2^l$ -pole moments: quadrupole ( $\Theta$ ), octopole ( $\Omega$ ), and hexadecapole ( $\Phi$ ), each, respectively, described by rank  $l=2, 3, 4$  tensors. Take, for example, the second-rank Cartesian tensor  $P_{ij} \equiv i \cdot j = \int i \cdot j (\Psi_\Lambda^* \Psi_\Lambda) dV$ , where its components are electric moments calculated as expectation values of the product of any two Cartesian coordinates  $i, j=x, y, z$ . The

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anisotropy of property  $P$  in the  $xy$  plane can be investigated by asking for which state it holds that  $P_{xx}=P_{yy}$  and for which  $P_{xx}\neq P_{yy}$ . Such question is valid since—as will be shown later—there exists a connection between state symmetry ( $\Lambda$ ) and the  $n$  value of each multipole.

A few comments about electric  $2^l$ -pole moments (discounting the dipole) are relevant. First, they are usually determined indirectly via low accuracy methods. Details on all components are rare, with the available data generally limited to average values. Secondly, experimental multipoles for degenerate states are scarce.<sup>3,5,12</sup> As a case in point, only the average  $\langle\Theta\rangle$  is known even for  $\text{NO}(X^2\Pi)$ .<sup>13</sup> Needless to say, experimental multipoles for  $\Delta$ ,  $\Phi$ , and  $\Gamma$  states of main-group molecules practically do not exist.<sup>3,5,12</sup> The bulk of the present knowledge on electric multipoles stems from theoretical studies, which, as said above, have assumed that all linear states—*degenerate* and *nondegenerate*—exhibit a common behavior.

The paper is organized as follows. Section II gives a brief account on the discrepancies in the literature about the  $n$  value. Section III deals with general properties of traceless tensors, which are later applied in Sec. IV to the  $\Theta$ ,  $\Omega$ , and  $\Phi$  moments calculated for a variety of states and radicals (the latter in parentheses):  $X^2\Sigma^+(\text{CN})$ ,  $X^2\Pi(\text{NO})$ ,  $a^3\Pi(\text{C}_2)$ ,  $X^2\Delta(\text{NiH})$ ,  $X^3\Delta(\text{TiO})$ ,  $X^3\Phi(\text{CoF})$ , and  $X^4\Phi(\text{TiF})$ . An overview of the more important findings is presented in Sec. V.

## II. HISTORICAL BACKGROUND

We give here a brief historical summary on the discrepancies about the number ( $n$ ) of constants needed to describe tensor properties in degenerate states. Spectroscopy studies<sup>1,2</sup> on the hyperfine structure reported coupling constants for *magnetic* ( $T_{ij}$ ) and *electric* interactions (nuclear-quadrupole  $eQq_{ij}$ ). Since  $T_{ij}$  and  $eQq_{ij}$  are traceless tensors ( $T_{xx}+T_{yy}+T_{zz}=0$ ), their  $n$  value is one unit less than for a traced tensor.<sup>14</sup> Just from the beginning, it was established for  $\Sigma$  radicals that each hfcc is specified by *one* component,  $T_{zz}$  or  $q_{zz}$ . The situation is different for  $\Pi$  states: Frosch and Foley<sup>15</sup> had to include in the Hamiltonian an azimuthal term  $e^{i2\varphi}$  to describe the mixing between  $\Lambda=+1$  and  $\Lambda=-1$  components. Thus *two* hfcc's are needed:  $T_{zz}$  and  $(T_{xx}-T_{yy})$ ; and  $q_{zz}$  and  $(q_{xx}-q_{yy})$ .<sup>1,2</sup> Electron spin resonance studies also determined traced  $g$  tensors, which parameterize the *magnetic* dipole moment ( $\mu^M$ ).<sup>1,2,16</sup> Again,  $\Sigma$  and  $\Pi$  behave differently: *two* independent  $\mu^M$ 's are required for  $\Sigma$  [ $(\mu^M)_{\parallel}$  and  $(\mu^M)_{\perp}=(\mu^M)'_{\perp}$ ] but *three* for  $\Pi$  states [ $(\mu^M)_{\parallel}$ ,  $(\mu^M)_{\perp}$ , and  $(\mu^M)'_{\perp}$ ].

Experiments of a different nature carried out in the 1970s—namely, collision reactions (e.g.,  $\text{H}+\text{NO}_2\rightarrow\text{OH}+\text{NO}$ )<sup>17</sup> and photodissociation processes ( $\text{H}_2\text{O}\rightarrow\text{OH}+\text{H}$ )<sup>18</sup>—investigated the charge distributions of  $\Pi$  radicals (via multipole expansions describing intermolecular interactions)<sup>19</sup> and found that  $\Pi$ -type CDD's are axially asymmetric. For details, see the papers of Alexander and Dagdigian, and Zare and co-worker.<sup>20,21</sup> Despite the above findings, several works published in the 1990s—mostly *ab initio* calculations of potential surfaces [e.g.,  $\text{N}_2^+(\text{A}^2\Pi_u)+\text{He}$  (Ref. 11) and  $\text{OH}(X^2\Pi)+\text{Ar}$ ]<sup>22</sup>—continued on assigning to  $\Pi$  states one quadrupole ( $\Theta_{\parallel}$ ) and two polarizabilities

( $\alpha_{\parallel}, \alpha_{\perp}$ ), as if they were axially symmetric. A recent study<sup>23</sup> on the reaction  $\text{OH}(X^2\Pi)+\text{HCl}(X^1\Sigma^+)$ , however, correctly assigns *two* independent  $\theta$  and  $\Omega$  components to OH.

Electric  $2^l$  poles have mostly been studied theoretically. Buckingham<sup>3</sup> determined multipole  $n$  values via group theory. Other authors also studied the restrictions upon  $n$ .<sup>4,5</sup> There even exists a theorem proving that “only *one* independent scalar quantity is required to determine a molecular electric multipole tensor of rank  $l$  for molecules with an  $n$ -fold axis of symmetry where  $l<n$ .” Thus,  $n=1$  for *any*  $2^l$  pole of all linear molecules, a rule invoked in most calculations published to date, including those on degenerate states.<sup>9–11</sup> A study by Gwinn *et al.*<sup>24</sup> showed that  $\langle x^2\rangle\neq\langle y^2\rangle$  for  $\text{OH}(X^2\Pi)$ , but its implication upon the quadrupole moment was later generally ignored (same observation applies to the polarizability  $\alpha$ ).

## III. IRREDUCIBLE CARTESIAN MULTIPOLE TENSORS AND SYMMETRY CONSIDERATIONS

The quantum mechanical evaluation of expectation values requires two quantities, the operator  $\mathbf{P}$  and wave function  $\Psi_{\Lambda}$  (the  $\Lambda$  label characterizes a given linear state), according to

$$\langle\mathbf{P}\rangle\equiv\int\Psi_{\Lambda}^*(\mathbf{P})\Psi_{\Lambda}dV. \quad (1)$$

$\mathbf{P}$  is the operator representing electric  $2^l$  poles. The  $\Psi_{\Lambda}$ 's form bases for irreducible representations of the  $C_{\infty v}$  point group, so that it is desirable for  $\mathbf{P}$  to be also described by symmetry-adapted components. Part A below analyzes Cartesian tensors in their reducible and irreducible forms, where the latter are more appropriate to discuss symmetry properties (the linear  $C_{\infty v}$  point group is assumed throughout). In part B, group theory arguments are presented to decide on the value of  $n$  for  $2^l$  poles of  $\Sigma$ ,  $\Pi$ ,  $\Delta$ , and  $\Phi$  electronic states.

### A. Reducible and irreducible Cartesian tensors

We consider first a second-rank tensor, and extend later the analysis to higher ranks. In the following,  $P_{ij}$  stands for the reducible Cartesian component of a second-rank property, like the traced electric second moments  $i\cdot j\equiv\int i\cdot j(\Psi_{\Lambda}^*\Psi_{\Lambda})dV$  ( $i,j=x,y,z$ ) or any traceless property ( $\Theta_{ij}, T_{ij}, q_{ij}$ ). The  $(2p+1)$  components of an irreducible Cartesian tensor of rank  $p$  are labeled as  $P_m^{(p)}$ , with  $m$  ranging from  $-p$  to  $p$ . From the theory of irreducible tensors,<sup>25,26</sup> relevant properties are as follows: (i) a *reducible* Cartesian tensor of rank  $l$  can be decomposed as a linear combination of *irreducible* Cartesian tensors ( $P_m^{(p)}$ ) of increasing rank  $p$ , up to a maximum  $p=l$ ,

$$P_{ij\cdots kl}(\text{lth-rank Cartesian, reducible}) \\ = a_0 P_m^{(0)} + a_1 P_m^{(1)} + a_2 P_m^{(2)} + \cdots + a_l P_m^{(l)}$$

(for odd  $l$ ,  $a_0=0$ ); and (ii) the expansion contains only one irreducible tensor of the highest rank  $l$  (the last coefficient,  $a_l=1$  for all  $l$ ), and which is *symmetric* and *traceless* in any

TABLE I. Relations between reducible ( $P_{ij}$ ) and irreducible ( $P_m^{(l)}$ ) components of a symmetric cartesian tensor  $\mathbf{P}$  of rank  $l=2$ , and its particular application to linear molecules ( $C_{\infty v}$ ).

Reducible ( $P_{ij}$ ) <sup>c</sup>	Tensor components <sup>a</sup> Irreducible <sup>b</sup> ( $P_m^{(p)}$ ) <sup>d</sup>	Irreducible $\Rightarrow$ Symmetric $P^b$ ( $P_{ij}=P_{ji}$ )	Irreducible $\Rightarrow$ Symmetric $\Rightarrow$ Linear [ $C_{\infty v}$ ] <sup>b</sup> [ $P_{\alpha\alpha}=0(\alpha=x,y)$ ]
$P_{xx} \ P_{xy} \ P_{xz}$	$P_0^{(0)}=q[P_{zz}+(P_{xx}+P_{yy})]$	$P_0^{(0)}=q[P_{zz}+(P_{xx}+P_{yy})]$	$P_0^{(0)}=q[P_{zz}+(P_{xx}+P_{yy})]$
$P_{yx} \ P_{yy} \ P_{yz}$	$P_0^{(1)}=r[P_{xy}-P_{yx}]$	$P_0^{(1)}=0$	$P_0^{(1)}=0$
$P_{zx} \ P_{zy} \ P_{zz}$	$P_{\pm 1}^{(1)}=-s[P_{zx}-P_{xz}\pm i(P_{zy}-P_{yz})]$	$P_{\pm 1}^{(1)}=0$	$P_{\pm 1}^{(1)}=0$
	$P_0^{(2)}=t[3P_{zz}-(P_{xx}+P_{yy}+P_{zz})]^c$	$P_0^{(2)}=t[3P_{zz}-(P_{xx}+P_{yy}+P_{zz})]^c$	$P_0^{(2)}=t[3P_{zz}-(P_{xx}+P_{yy}+P_{zz})]^c$
	$P_{\pm 1}^{(2)}=\mp s[P_{xz}+P_{zx}\pm i(P_{yz}+P_{zy})]$	$P_{\pm 1}^{(2)}=\mp 2s[P_{xz}\pm i(P_{yz})]$	$P_{\pm 1}^{(2)}=0$
	$P_{\pm 2}^{(2)}=s[(P_{xx}-P_{yy})\pm i(P_{xy}-P_{yx})]$	$P_{\pm 2}^{(2)}=s[(P_{xx}-P_{yy})\pm i(2P_{xy})]$	$P_{\pm 2}^{(2)}=s[(P_{xx}-P_{yy})\pm i(2P_{xy})]^f$

<sup>a</sup>No symmetry restrictions (valid for any point group). Normalization factors:  $q=-(1/\sqrt{3})$ ,  $r=-(i/\sqrt{2})$ ,  $s=\frac{1}{2}$ , and  $t=1/\sqrt{6}$ .

<sup>b</sup>For a second rank traceless tensor ( $P_{zz}+P_{xx}+P_{yy}=0$ ) it holds throughout that  $P_0^{(0)}=0$  and  $P_0^{(2)}=(3t)P_{zz}$ .

<sup>c</sup> $3^{(l=2)}=9$  reducible Cartesian components.

<sup>d</sup> $p=0,1,2(=l)$ ;  $m$  ranges from  $-p$  to  $p$  [ $(2p+1)$  components]. All  $(p,m)$  combinations give nine irreducible Cartesian components.

<sup>e</sup>Rearranging,  $P_0^{(2)}=(2t)[P_{zz}-(P_{xx}+P_{yy})/2]$ .

<sup>f</sup>Real [ $P_{\pm 2}^{(2)}$ ] $=(1/2)[P_{+2}^{(2)}+P_{-2}^{(2)}]\propto(P_{xx}-P_{yy})$ . Examples:  $(\Theta_{xx}-\Theta_{yy})$  for quadrupole moment;  $d=T_{xx}-T_{yy}$  and  $q_2=(q_{xx}-q_{yy})$  for hfcc's;  $(\alpha_{xx}-\alpha_{yy})$  for dipole polarizability.

pair of Cartesian subindices (such rank- $l$  tensor is said to be in its “natural” form).<sup>25,26</sup>

Of importance for  $2^l$  poles is the connection between a *reducible* Cartesian tensor of rank  $l$  with  $3^l$  components [e.g.,  $l$ th-electric moments  $x^p y^q z^r$  ( $l=p+q+r$ )] versus its “natural” *irreducible* Cartesian counterpart  $P_m^{(l)}$  with  $(2l+1)$  independent members. Additional constraints—imposed by tensor structure, molecular point group, and state symmetry ( $\Lambda$ )—will further reduce such  $(2l+1)$  degree of freedom to the final  $n$  value searched here for linear states with different  $\Lambda$ 's.

Table I describes the conversion of the nine components of a second-rank tensor from its reducible Cartesian form  $P_{ij}$  ( $i,j=x,y,z$ ) (first column) to its irreducible representation  $P_m^{(p)}$ . The second column gives the general situation, the third considers a symmetric tensor ( $P_{ij}=P_{ji}$ ), while the last column applies to linear molecules.  $P_m^{(p)}$  components—which transform like the spherical harmonics  $Y_m^p$ —are expressed as linear combinations of the nine Cartesian  $P_{ij}$  components.  $P_{0,\pm 1}^{(1)}$  vanishes for a symmetric tensor ( $P_{ij}=P_{ji}$ ). In  $C_{\infty v}$ , it holds  $P_{xz}=P_{yz}=0$ , so that  $P_{\pm 1}^{(2)}$  also vanishes. The (real) nonzero set is  $P_0^{(0)}=-(1/\sqrt{3})[P_{xx}+(P_{yy}+P_{zz})]$ ,  $P_0^{(2)}=(1/\sqrt{6})\times[2P_{zz}-(P_{xx}+P_{yy})]$ , and  $P_{\pm 2}^{(2)}=(1/2)[P_{xx}-P_{yy}]$ . Hereafter, normalization factors will be left out.

The three nonzero terms in Table I (fourth column) form bases for irreducible representations (Irrep) of  $C_{\infty v}$ : [ $P_0^{(0)}, P_0^{(2)}$ ] for  $\Sigma^+$ , and [ $P_{\pm 2}^{(2)}$ ] for  $\Delta$ .<sup>27–29</sup> In  $C_{2v}$  symmetry, there are *three* totally symmetric  $A_1$  terms ( $[P_{zz}+(P_{xx}+P_{yy})]$ ,  $[2P_{zz}-(P_{xx}+P_{yy})]$ , and  $[(P_{xx}-P_{yy})]$ ), and *one*  $A_2[P_{xy}]$ . Note that  $A_1[(P_{xx}-P_{yy})]$  and  $A_2[P_{xy}]$  are, respectively, the real (Re) and imaginary members of  $\Delta$ . We deal here only with real operators and wave functions.

The crux of our analysis is simple:  $n$  is equal to the number of nonzero  $P_m^{(l)}$  components. Thus, for linear molecules, a maximum  $n=3$  applies to any traced second-rank tensor. For a traceless tensor ( $P_0^{(0)}=[P_{zz}+(P_{xx}+P_{yy})]=0$ ) the maximum value is  $n=2$  (like  $\Theta_{ij}, T_{ij}, q_{ij}$ ). This can be further lowered to  $n=1$  only if the irreducible component ( $P_{xx}-P_{yy}$ ) vanishes.

Table II gives the relations between reducible and irreducible Cartesian components for traceless tensors of rank 2–4.<sup>27–30</sup> For  $C_{\infty v}$  systems, only components with (even)  $m=0,2,4,\dots$  are nonzero. The relevant tensor/operator components  $P_m^{(l)}$  are as follows: (a)  $P_{m=0}^{(l)}$ , the “parallel” component, which is different from zero, *always*; (b)  $P_{m=\pm 2}^{(l)}$ , with a nonzero Cartesian expansion for  $l\geq 2$ ; and (c)  $P_{m=\pm 4}^{(l)}$ , with a nonzero Cartesian  $P_{ijkl}$  expansion for  $l\geq 4$  (hexadecapole and above).

At this point, the following conclusions about  $n$  can be put forward. When  $n=1$ , for any  $l$  value, the independent term is  $P_0^{(l)}$ , the parallel component. If  $n=2$  but  $l=2,3$ , the second free parameter is  $P_{\pm 2}^{(2 \text{ or } 3)}$ . The situation becomes more complex for  $n=2$  and  $l\geq 4$ , since either  $P_{\pm 2}^{(4)}$  or  $P_{\pm 4}^{(4)}$  can be nonzero: which components survive is determined by the value of  $\Lambda$  (Sec. III B).

The material in Table II below the headings  $r^l Y_m^l(x,y,z)$  and  $Y_m^l(\theta, \varphi)$  helps us to rationalize the various CDD asymmetries. In the Cartesian representation  $Y_m^l(x,y,z)$ , it is seen for even  $|m|=2,4$  that  $Y_m^l$  contains the term  $(x\pm iy)^2$ —as in  $P_{\pm 2}^{(2)}$  and  $P_{\pm 2}^{(3)}$ —or its square  $(x\pm iy)^4$ , as in  $P_{\pm 4}^{(4)}$ . For their representations  $Y_m^l(\theta, \varphi)$  in angular variables (Table II), terms describing the deviation from axial symmetry are those dependent on the angle  $\varphi$  (in Table II, the underlined components containing  $[\sin^2 \theta \cdot e^{\pm 2i\varphi}]$  or  $[\sin^4 \theta \cdot e^{\pm 4i\varphi}]$ ). The factor  $(\sin^2 \theta)$  gives the projection onto the  $(xy)$  plane, while  $(e^{\pm 2i\varphi})$  follows such projection along  $\varphi$  (rotation around  $z$ ), i.e., *both terms* conjunctionally scan the rotational symmetry of CDD in the  $(xy)$  plane perpendicular to  $z$ .

The results above can be generalized in two directions. First, an axially symmetric CDD (found *exclusively* in  $\Sigma$  states with no  $\varphi$  dependence) implies that the  $Y_m^l$  functions (or  $2^l$  poles) should obey the equality  $(x+iy)^m=0$  [ $|m|=2,4,6,\dots$ ], that is, both Re and Im parts vanish for even  $m$ . For second moments,  $(x+iy)^2=[(x^2-y^2)+i(2xy)]$ , so that axial symmetry is equivalent to  $x^2=y^2$  at the quadrupole level (real  $\psi$ ). Similar  $(x+iy)^m$  expansions for a particular combination of  $2^l$  poles and states (i.e., of  $l$  and  $\Lambda$  values) allow us to find how Cartesian moments of a general type



TABLE II. Nonzero components of irreducible Cartesian tensors of second to fourth rank ( $l=2,3,4$ ), and its particular application to linear molecules ( $C_{\infty v}$ ).

$l$	Nonzero <sup>a</sup> moments	$[P_m^{(l)}]^b$	$\Gamma_{\text{irr}}^c$ $C_{\infty v}(C_{2v})$	Real part <sup>d</sup> proportional to	$\propto r^l Y_{lm}(x, y, z)^e$	$\propto Y_{lm}(\Theta, \varphi)^f$
2	zz, xx, yy	$P_0^{(2)}$ $P_{\pm 2}^{(2)}$	$\Sigma^+(A_1)$ $\Delta(A_1, A_2)$	$[2P_{zz} - (P_{xx} + P_{yy})]$ $[(P_{xx} - P_{yy})]$	$(3z^2 - r^2)$ $(x \pm iy)^2$	$(3 \cos^2 \theta - 1)$ $\sin^2 \theta \cdot e^{\pm 2i\varphi}$
3	zzz, xxz, yyz	$P_0^{(3)}$ $P_{\pm 2}^{(3)}$	$\Sigma^+(A_1)$ $\Delta(A_1, A_2)$	$[2P_{zzz} - 3(P_{xxz} + P_{yyz})]$ $[(P_{xxz} - P_{yyz})]$	$z \cdot (5z^2 - 3r^2)$ $z \cdot (x \pm iy)^2$	$(2 \cos^3 \theta - 3 \cos \theta \sin^2 \theta)$ $\cos \theta \cdot \sin^2 \theta \cdot e^{\pm 2i\varphi}$
4	zzzz, xxxx, yyyy, xxzz, yyzz, xxyy	$P_0^{(4)}$ $P_{\pm 2}^{(4)}$ $P_{\pm 4}^{(4)}$	$\Sigma^+(A_1)$ $\Delta(A_1, A_2)$ $\Gamma(A_1, A_2)$	$[4P_{zzzz} + (3/2)(P_{xxxx} + P_{yyyy}) - 12(P_{xxzz} + P_{yyzz}) + 3P_{xxyy}]$ $[(P_{xxxx} - P_{yyyy}) - 6(P_{xxzz} - P_{yyzz})]$ $[(P_{xxxx} + P_{yyyy}) - 6P_{xxyy}]$	$(35z^4 - 30z^2r^2 + 3r^4)$ $(7z^2 - r^2) \cdot (x \pm iy)^2$ $(x \pm iy)^4$	$(35 \cos^4 \theta - 30 \cos^2 \theta + 3)$ $(7 \cos^2 \theta - 1) \cdot \sin^2 \theta \cdot e^{\pm 2i\varphi}$ $[\sin^2 \theta \cdot e^{\pm 2i\varphi}]^2$

<sup>a</sup>lth (second, third, fourth)-Cartesian moments  $\langle x^p y^q z^r \rangle_f = \langle x^p y^q z^r \rangle \rho dv$  ( $l=p+q+r$ ). Here, zz, xxz, xxyy, etc. (or  $z^2 x^2 z^2, x^2 y^2$ , etc.), stand for  $\langle zz \rangle$ ,  $\langle xxz \rangle$ ,  $\langle xxyy \rangle$ , etc., respectively.

<sup>b</sup>For  $P_m^{(l)} \equiv \langle \Psi_\Lambda | P_m^{(l)} | \Psi_\Lambda \rangle$ , it holds: (i)  $P_0^{(l)} \neq 0$  for any  $\Lambda$ ,  $l$ ; (ii)  $P_2^{(l)} \neq 0$  for  $\Pi(\Lambda=1)$  and  $l \geq 2$ ; (iii)  $P_4^{(l)} \neq 0$  for  $\Delta(\Lambda=2)$  and  $l \geq 4$ .

<sup>c</sup> $\Gamma_{\text{irr}}$  (irreducible rep.) according to which  $P_m^{(l)}$  transforms. Using  $(C_{2v})$  real wave functions, only  $A_1$  components are of interest.

<sup>d</sup>Totally symmetric ( $\Sigma^+, A_1$ ) combinations of Cartesian  $P_{ij}$ 's, equal to  $(P_m^{(l)} + P_{-m}^{(l)})/2$  between irred.  $P_m^{(l)}$  components ( $m \neq 0$ ).

<sup>e</sup>Expanding these solid spherical harmonics (irreducible tensor components) in Cartesian coordinates ( $x, y, z$ ) gives symmetry adapted (imaginary) linear combinations of  $x^p y^q z^r$  monomials ( $l=p+q+r$ ), the latter having the same composition as in column 2.

<sup>f</sup>Underlined factors highlight the dependency of  $P_m^{(l)}$  on the azimuthal angle  $\varphi$ . Their real parts  $\cos(m\varphi)$  [ $|m|=2, 4$ ] are proportional to the characters of the  $\Delta$  and  $\Gamma$  representations of the  $C_{\infty v}$  group.

$x^p y^q z^r$  ( $l=p+q+r$ ) are interrelated among themselves (see Appendix A).

As a second generalization,  $P_{\pm 6}^{(6)}$  [ $2^6$  pole] is proportional to  $(x \pm iy)^6$ , or to  $[\sin^6 \theta \cdot e^{\pm 6i\varphi}]$ . The first relation allows us to derive  $P_{\pm 6}^{(6)}$  as a linear combination of Cartesian  $x^p y^q z^r$  moments ( $p+q+r=6$ ). Note that  $P_{\pm 6}^{(6)}$  is nonzero only for  $\Phi(\Lambda=3)$ , and higher, states. (See Ref. 31 for expansions of  $P_m^{(l)}$  in Cartesian and spherical coordinates.) If desired, explicit expressions for the multipole components  $P_{\pm 2}^{(6)}$  and  $P_{\pm 4}^{(6)}$ —which are nonzero for  $\Pi$  and  $\Delta$  states, respectively—are obtained by expanding those  $Y_m^{(6)}$  harmonics containing the factors  $(x \pm iy)^2$  and  $(x \pm iy)^4$ .

Another piece of information displayed in Table II is extremely valuable:  $P_m^{(l)}$  for even  $|m|=0, 2, 4$  transforms, respectively, like the  $\Sigma^+$ ,  $\Delta$ , and  $\Gamma$  Irrep's of the  $C_{\infty v}$  point group. These symmetry properties are of relevance for the discussion to follow.

## B. Symmetry considerations

We study here which states give  $P_m^{(l)} \neq 0$  for  $m=0, 2, 4, 6, \dots$ . The goal is to find, using group theory arguments, which *nonvanishing irreducible tensor components* ( $P_0^{(l)}, P_{\pm 2}^{(l)}, P_{\pm 4}^{(l)}$ ) have *nonzero* matrix elements  $\langle \Psi_\Lambda | P_m^{(l)} | \Psi_\Lambda \rangle$  for a state  $\Psi_\Lambda$  of  $\Sigma^\pm$ ,  $\Pi$ ,  $\Delta$ , and  $\Phi$  symmetries. As said before, the number of nonzero matrix elements defines  $n$ , or as stated by Buckingham:<sup>3</sup> “The number of independent constants to describe a tensor property is the number of times the totally symmetric representation occurs in the irreducible form of the property appropriate to the particular symmetry group.” To determine  $n$  we shall use the direct product

$$[\Psi_\Lambda] \otimes [P_m^{(l)}] \otimes [\Psi_\Lambda] = [P_m^{(l)}] \otimes [\Psi_\Lambda \otimes \Psi_\Lambda], \quad (2)$$

where  $[\Psi_\Lambda]$  or  $[P_m^{(l)}]$  expresses the irreducible representation of the wave function  $\Psi_\Lambda$  or the  $P_m^{(l)}$  component of the multipole operator. In general, Eq. (2) gives a reducible representation ( $\Gamma_{\text{red}}$ ) decomposable into irreducible representations ( $\Gamma_{\text{irr}}$ ). Of major interest are those cases where

$$\begin{aligned} \Gamma_{\text{red}}\{[P_m^{(l)}] \otimes [\Psi_\Lambda \otimes \Psi_\Lambda]\} \\ = \Gamma_{\text{irr}}(\Sigma^+) + [\text{other } \Gamma_{\text{irr}}(\text{non-}\Sigma^+) \text{ 's}]. \end{aligned} \quad (3)$$

If  $\Gamma_{\text{red}}$  contains the totally symmetric representation  $\Gamma_{\text{irr}}(\Sigma^+)$  of  $C_{\infty v}$  then  $\langle \Psi_\Lambda | P_m^{(l)} | \Psi_\Lambda \rangle$  is nonzero.<sup>32</sup> In Eqs. (2) and (3), the symmetries of two different entities are compounded: one pertains to the operator  $P_m^{(l)}$  and the other to the state ( $\Lambda$ ) investigated.

Since the nonzero components  $P_m^{(l)}$  ( $l=2, 3, 4$ ) transform as  $\Sigma$ ,  $\Delta$ , and  $\Gamma$  (Table II), the direct product Eq. (2) can be nonzero for each of the following cases with  $|m|=0, 2, 4$ , namely, (a)  $|m|=0$ : for  $P_0^{(2)}, P_0^{(3)}, P_0^{(4)}$ —all  $\Gamma_{\text{irr}}(\Sigma^+)$  species—only if  $\Gamma_{\text{red}}[\Psi_\Lambda \otimes \Psi_\Lambda]$  contains  $\Gamma_{\text{irr}}(\Sigma^+)$ ; (b)  $|m|=2$ : for  $P_{\pm 2}^{(2)}, P_{\pm 2}^{(3)}, P_{\pm 2}^{(4)}$ —all  $\Gamma_{\text{irr}}(\Delta)$  species—only if  $\Gamma_{\text{red}}[\Psi_\Lambda \otimes \Psi_\Lambda]$  contains  $\Gamma_{\text{irr}}(\Delta)$ ; and (c)  $|m|=4$ : for  $P_{\pm 4}^{(4)}$ —a  $\Gamma_{\text{irr}}(\Gamma)$  species—only if  $\Gamma_{\text{red}}[\Psi_\Lambda \otimes \Psi_\Lambda]$  contains  $\Gamma_{\text{irr}}(\Gamma)$ .

In the following, cases (a)–(c) will be discussed individually.

*Case (a)* The  $|m|=0$  operators  $P_0^{(2)}, P_0^{(3)}$ , and  $P_0^{(4)}$  transform like  $\Sigma^+$ , so that  $\langle \Psi_\Lambda | P_0^{(l)} | \Psi_\Lambda \rangle \neq 0$  for *any linear state*  $\Psi_\Lambda$  (i.e., regardless of its  $\Lambda$  value) since  $\Gamma_{\text{red}}[\Psi_\Lambda \otimes \Psi_\Lambda]$  *always contains*  $\Gamma_{\text{irr}}(\Sigma^+)$ .<sup>32</sup>

*Case (b)*  $\Gamma_{\text{red}}[\Psi_\Lambda \otimes \Psi_\Lambda]$  contains  $\Gamma_{\text{irr}}(\Delta)$  only if  $\Psi_\Lambda \equiv \Pi$ , according to  $\Gamma_{\text{red}}[\Pi \otimes \Pi] = \Delta + \Sigma^+ + \Sigma^-$ .<sup>32</sup> Therefore, for the second to fourth rank multipoles studied here, the matrix elements of  $P_{\pm 2}^{(l)}$  ( $l=2, 3, 4$ ) are nonzero *only* for  $\Pi$  states (actually, for all  $P_m^{(l)}$  components fulfilling  $l \geq 2$  and  $|m|=2$ ).

*Case (c)*  $\Gamma_{\text{red}}[\Psi_\Lambda \otimes \Psi_\Lambda]$  contains  $\Gamma_{\text{irr}}(\Gamma)$  only if  $\Psi_\Lambda \equiv \Delta$ , according to  $\Gamma_{\text{red}}[\Delta \otimes \Delta] = \Gamma + \Sigma^+ + \Sigma^-$ .<sup>32</sup> Thus, the  $P_{\pm 4}^{(l)}$  component (which exists for  $l$ th-rank tensors with  $l \geq 4$ ) only survives for  $\Delta$  states.

## C. Number of independent multipole components ( $n$ ): Its dependence on the $l$ and $\Lambda$ values

Table III lists the value of  $n$  for traceless  $2^l$  poles ( $l=1-9$ ) for linear ( $\Lambda=0-4$ ) states.  $\Sigma$  states are the only ones for which  $n=1$  for all  $2^l$  poles, i.e., each multipole is fully

TABLE III. Number of independent parameters ( $n$ ) needed to describe traceless electric  $2^l$ -pole moments of different electronic states in linear molecules ( $C_{\infty v}$ ).  $2^l$  poles in  $D_{\infty h}$  symmetry: same rules as  $C_{\infty v}$  for odd  $l$  ( $\Theta, \Phi, \xi^6$ ) but all zero for even  $l$  ( $\mu, \Omega, \xi^5$ ). 2 poles with  $l=5, 6, \dots$ , are here called  $\xi^5, \xi^6$  following Buckingham's [Ref. 3(d)] nomenclature  $\xi_{\alpha\beta\gamma\delta\epsilon}^{(5)}, \xi_{\alpha\beta\gamma\delta\epsilon\varphi}^{(6)}$ . Isnard *et al.* [Ref. 26(d)] used the symbols  $\Xi, \Gamma$ , and  $\Pi$  for the fifth- to seventh-rank multipoles.

State	$\Lambda$	$m'^a$ ( $=2\Lambda$ )	$l < 2\Lambda$	$n=1$ $P_0^{(l)} \neq 0^b$ component	$2^l$ -pole <sup>c</sup> involved	$l \geq 2\Lambda$	$n=2$ $P_0^{(l)}, P_m^{(l)} \neq 0^d$ components	$2^l$ -pole involved
$\Sigma^\pm$	0	0		$P_0^{(l)}$	$[\mu, \Theta, \Omega, \Phi, \dots]_{  }$			
$\Pi^e$	1	2	$l=1$	$P_0^{(1)}$	$[\mu]_{  }$	$l=2, 3, 4, \dots$	$P_0^{(2)}, P_0^{(3)}, P_0^{(4)}, \dots$	$[\Theta, \Omega, \Phi, \dots]_{  }$
$\Delta^{f,g}$	2	4	$l=1, 2, 3$	$P_0^{(1)}, P_0^{(2)}, P_3^{(3)}$	$[\mu, \Theta, \Omega]_{  }$	$l=4, 5, 6, \dots$	$P_2^{(2)}, P_2^{(3)}, P_2^{(4)}, \dots$	$[\Theta, \Omega, \Phi, \dots]_{\perp}$
$\Phi^g$	3	6	$l=1, 2, \dots, 5$	$P_0^{(1)}, \dots, P_0^{(5)}$	$[\mu, \Theta, \Omega, \Phi, \xi^5]_{  }$	$l=6, 7, 8, \dots$	$P_4^{(4)}, P_4^{(5)}, P_4^{(6)}, \dots$	$[\Phi, \xi^5, \xi^6, \dots]_{  }$
$\Gamma^g$	4	8	$l=1, 2, \dots, 7$	$P_0^{(1)}, \dots, P_0^{(7)}$	$[\mu, \Theta, \dots, \xi^6, \xi^7]_{  }$	$l=8, 9, \dots$	$P_6^{(6)}, P_6^{(7)}, P_6^{(8)}, \dots$	$[\xi^6, \xi^7, \xi^8, \dots]_{  }$
							$P_8^{(8)}, P_8^{(9)}, \dots$	$[\xi^8, \xi^9, \dots]_{\perp}$

<sup>a</sup>For  $\Lambda \neq 0$  states,  $m'$  identifies the  $P_{|m'|}^{(l)}$  component giving a *second* nonzero  $2^l$  pole, with  $l \geq 2\Lambda$ .

<sup>b</sup> $P_0^{(l)} \neq 0$  for all  $C_{\infty v}$  states (see also table heading).

<sup>c</sup>Each component ( $\mu_z, \Theta_{zz}, \Omega_{zzz}, \Phi_{zzzz}$ , etc.) customarily called the “parallel” component.

<sup>d</sup>Each entry, *first line*:  $P_0^{(l)}$  component (literature standard); *second line*: second nonzero  $P_{|m'|}^{(l)}$  component (this work).

<sup>e</sup> $P_2^{(l)}$  is proportional to  $(\Theta_{xx} - \Theta_{yy}), (\Omega_{xxz} - \Omega_{yyz}), (\Theta_{xxx} - \Theta_{yyy})$  for  $l=2, 3, 4$ , respectively.

<sup>f</sup> $P_4^{(4)}$  is proportional to  $[(\Phi_{xxx} + \Phi_{yyy}) - 6\Phi_{xyy}]$ .

<sup>g</sup>Treatments similar to footnotes e and f can be done for higher states/multipoles using the procedure discussed in the text, together with  $Y_m^{(l)}$  (up to  $l=9$ ) expressions from the literature (Ref. 31).

represented by  $P_0^{(l)}$  (e.g.,  $\mu_z, \Theta_{zz}, \Omega_{zzz}, \Phi_{zzzz}$ , etc.). For  $\Pi$  states,  $n=1$  only applies to the dipole moment ( $\mu_z$ ), while  $n=2$  holds for all  $l \geq 2$  poles. The two nonzero terms in  $\Pi$  states are  $P_0^{(l)}$  and  $P_2^{(l)}$  ( $l \geq 2$ ), with the former usually labeled as the *parallel* component ( $P_0^{(2)} \equiv \Theta_{zz} \equiv \Theta_{||}; P_0^{(3)} \equiv \Omega_{zzz} \equiv \Omega_{||}$ ). For any  $2^l$  pole ( $l \geq 2$ ), the second term with  $|m|=2$  [i.e.,  $P_2^{(l)}$ ] measures the anisotropy between in-plane ( $xy$ ) components. The  $\Pi$ -type anisotropies of the quadrupole, octopole, and hexadecapole are defined as  $\delta\Theta_{\Pi} \equiv \Theta_2^{(2)}$ ;  $\delta\Omega_{\Pi} \equiv \Omega_2^{(3)}$ ; and  $\delta\Phi_{\Pi} \equiv \Phi_2^{(4)}$ .

For  $\Delta$  ( $\Lambda=2$ ) states,  $n=1$  holds for  $\mu_z, \Theta_{zz}$ , and  $\omega_{zzz}$  but  $n=2$  applies to the hexadecapole  $\Phi$  ( $l=4$ ), with nonzero members  $\Phi_0^{(4)}$  and  $\Phi_4^{(4)}$ . The anisotropy for the hexadecapole of a  $\Delta$  state is given by  $\delta\Phi_{\Delta} \equiv \Phi_4^{(4)}$ . Note that terms such as  $\Theta_4^{(2)}$  and  $\Omega_4^{(3)}$  do not exist ( $|m|$  cannot be larger than  $l$ ). Moving forward with our analysis,  $\Phi$  ( $\Lambda=3$ ) states are such that  $n=1$  parameter is required up to the  $2^5$ -pole moment, but  $n=2$  constants are needed starting with the sixth-multipole ( $l=2\Lambda$ ), and the same applies to higher moments. Here, the lowest possible anisotropy of  $\Phi$  type corresponds to  $\delta\xi_{\Phi}^{(6)} \equiv \xi_{|m|=6}^{(6)}$ , where the nomenclature  $\xi_m^{(6)}$  is used for the sixth multipole (Table III).

As shown in Appendix B, there exists a simple relation between  $(l, m)$  of  $P_{|m|}^{(l)}$  and the quantum number  $\Lambda$  [both  $\Lambda$  and  $m$  (given as  $|m|$ ) are unsigned parameters]. The general rule for a given  $\Lambda$  (state) is that  $P_{|m|}^{(l)} \neq 0$  only if  $|m|=2\Lambda$ , which in turns implies that the rank of the operator should be  $l \geq 2\Lambda$ . In other words, for a given ( $C_{\infty v}$ ) state with  $\Lambda \neq 0$ , the change from  $n=1$  to  $n=2$  begins at the  $2^l$  pole with  $l=2\Lambda$ . Thus, the *degree* of deviation from axial symmetry in  $\Pi, \Delta, \Phi$ , and  $\Gamma$  states can only be revealed by investigating  $2^l$  poles of increased complexity.

#### IV. QUADRUPOLE, OCTOPOLE, AND HEXADECAPOLE MOMENTS: $\Sigma$ STATES (CYLINDRICALLY SYMMETRIC) VERSUS $\Pi, \Delta$ , AND $\Phi$ STATES (CYLINDRICALLY ASYMMETRIC)

##### A. Cartesian moments, and traceless and irreducible electric $2^l$ -pole moments

The electric moments of a given CDD can be equivalently described by the following:

- Cartesian moments*  $\langle x^p y^q z^r \rangle$  ( $l=p+q+r$ ), as, for example,  $\langle xy \rangle, \langle xyz \rangle, \langle xxyz \rangle$  for  $l=2, 3, 4$ ;
- traceless Cartesian  $2^l$ -pole moments*, as defined by Buckingham<sup>3</sup> (quadrupole  $\Theta_{ij}$ , octopole  $\Omega_{ijk}$ , hexadecapole  $\Phi_{ijkl}$ , for  $l=2, 3, 4$ ); they vanish for a spherically symmetric CDD; and
- irreducible multipole moments*  $P_m^{(l)}$  proportional to  $r^l Y_m^{(l)}(\theta, \varphi)$ ,<sup>25,26</sup> introduced in Sec. III A. Quantum chemical programs first calculate the moments (a), which are thereafter transformed to representation (b). The advantage of (c) is the use of group theory arguments to their full extent (Sec. III B). A component of a Cartesian moment of order  $l$  is given by the expectation value

$$\langle x^p y^q z^r \rangle = \int d\nu \rho x^p y^q z^r \quad (l=p+q+r). \quad (4)$$

Here,  $\rho$  is the CD at point  $(x, y, z)$ ; each  $(x^p y^q z^r)$  monomial is relative to a molecule-fixed system of coordinates with its origin on the  $z$  axis, usually the center of mass. Cartesian moments such as  $\langle xx \rangle, \langle xxy \rangle$ , and  $\langle yyyy \rangle$  are written as  $x^2, x^2 y$ , and  $y^4$ . The expectation values  $x^2, y^2, x^4, y^4$ , and  $x^2 y^2$  are calculated with the *electronic* CD; those containing  $z^r$  ( $r=1-4$ ) have *nuclear and electronic* contributions. We use throughout Buckingham's traceless  $2^l$ -pole moments,<sup>3</sup> with

TABLE IV. Cartesian components  $\Theta_{ij}$  and  $\Omega_{iiz}$  of the traceless quadrupole  $\Theta$  and octopole  $\Omega$  moments of linear ( $C_{\infty v}$ ) molecules in terms of second- and third-electric moments. The last column displays the real parts of the nonzero irreducible  $P_m^{(2,3)}$  components  $\Theta_{0,2}^{(2)}$  and  $\Omega_{0,2}^{(3)}$ .  $zz(z^2)$  stands for  $\langle zz \rangle = \int (zz) \rho dv$ ;  $yyz(y^2z)$  for  $\langle yyz \rangle = \int (yyz) \rho dv$ , etc.

Quadrupole <sup>a</sup>	$zz$ ( $z^2$ )	$xx$ ( $x^2$ )	$yy$ ( $y^2$ )	Irreducible multipole components <sup>b</sup>
$\Theta_{zz}$	1	-1/2	-1/2	$\Theta_0^{(2)} \propto [z^2 - (x^2 + y^2)/2]_{\parallel}$
$\Theta_{xx}$	-1/2	1	-1/2	$\Theta_2^{(2)} \propto [(x^2 - y^2)/2]_{\perp}$
$\Theta_{yy}$	-1/2	-1/2	1	
Octopole <sup>c</sup>	$zzz$ ( $z^3$ )	$xxz$ ( $x^2z$ )	$yyz$ ( $y^2z$ )	
$\Omega_{zzz}$	1	-3/2	-3/2	$\Omega_0^{(3)} \propto [z^3 - 3(x^2z + y^2z)/2]_{\parallel}$
$\Omega_{xxz}$	-1/2	2	-1/2	$\Omega_2^{(3)} \propto [5(x^2z - y^2z)/2]_{\perp}$
$\Omega_{yyz}$	-1/2	-1/2	2	

<sup>a</sup> $\Theta_{zz} = [z^2 - 1/2(x^2 + y^2)]$ , etc.  $\Theta_{zz} = -(\Theta_{xx} + \Theta_{yy})$ , all states/point groups. Anisotropy  $\delta\Theta_{\Pi} = |\Theta_{xx} - \Theta_{yy}| = (3/2)|(x^2 - y^2)|$ , proportional to  $\Theta_2^{(2)}$ . Non- $\Pi$  states:  $(x^2 = y^2)$ ,  $\delta\Theta_{\Pi} = 0$  and  $\Theta_{xx} = \Theta_{yy} = -\Theta_{zz}/2$ .

<sup>b</sup>Nonzero (real) irreducible multipole components (parallel,  $m=0$ ; and perpendicular,  $|m|=2$ ).

<sup>c</sup> $\Omega_{zzz} = [z^3 - 3/2(x^2z + y^2z)]$ , etc.  $\Omega_{zzz} = -(\Omega_{xxz} + \Omega_{yyz})$ , all states/point groups. Anisotropy  $\delta\Omega_{\Pi} = |\Omega_{xxz} - \Omega_{yyz}| = (5/2)|(x^2z - y^2z)|$ , proportional to  $\Omega_2^{(3)}$ . Non- $\Pi$  states:  $(x^2z = y^2z)$ ,  $\delta\Omega_{\Pi} = 0$  and  $\Omega_{xxz} = \Omega_{yyz} = -\Omega_{zzz}/2$ .

Cartesian components (using McLean and Yoshimine's nomenclature<sup>6</sup>) as follows:

Quadrupole ( $l=2$ ):

$$\Theta_{zz} = \int dv \rho r^2 P_2(z/r) \propto [P_0^{(2)}], \quad (5a)$$

Octopole ( $l=3$ ):

$$\Omega_{zzz} = \int dv \rho r^3 P_3(z/r) \propto [P_0^{(3)}], \quad (5b)$$

$$\Omega_{xxz} = (1/2) \int dv \rho (5x^2z - zr^2), \quad (5c)$$

Hexadecapole ( $l=4$ ):

$$\Phi_{zzzz} = \int dv \rho r^4 P_4(z/r) \propto [P_0^{(4)}], \quad (5d)$$

$$\Phi_{xxzz} = (1/2) \int dv \rho r^4 [P_4(y/r) - P_4(x/r) - P_4(z/r)], \quad (5e)$$

where  $r$  is the distance to the origin. The  $l$ th-degree Legendre polynomial  $P_l(t)$  reads  $(3t^2 - 1)/2$  for  $l=2$ ;  $(5t^3 - 3t)/2$  for  $l=3$ ; and  $(35t^4 - 30t^2 + 3)/8$  for  $l=4$ , and the variable  $t$  stands for  $x/r$ ,  $y/r$ , and  $z/r$ . Components not listed are obtained by appropriate substitutions of the  $(x, y, z)$  coordinates.

**Quadrupole moment.** Table IV lists the expansion coefficients for  $\Theta_{ij}$  and  $\Omega_{iiz}$  components ( $i=x, y, z$ ), in terms of Cartesian moments [as defined by Eqs. (5a)–(5c)]. The real parts of the irreducible components are also given for  $l=2, 3$  and  $|m|=0, 2$  (cf. Tables I and II).

For states obeying the equality  $x^2 = y^2$  (*non- $\Pi$*  states), it holds that  $\Theta_{zz} = (z^2 - x^2)$ , that is,  $\Theta_{zz}$  contrasts the parallel ( $z^2$ ) and perpendicular ( $x^2, y^2$ ) moments. Also,  $\Theta_{xx} = \Theta_{yy} = -\Theta_{zz}/2 = -(z^2 - x^2)/2$ , so that  $n=1$  for the quadrupole for any state with  $\Lambda \neq 1$ . On the other hand, very little has been discussed in the literature about the situation when  $x^2 \neq y^2$ . A

full description of such cases requires *two* quadrupole components, let us say,  $(z^2 - x^2)$  and  $(z^2 - y^2)$ , or for that matter, *any suitable pair of independent functions* on the  $(x^2, y^2, z^2)$  variables. It always holds for any linear state that  $\Theta_{zz}(\Theta_{\parallel}) = [z^2 - (x^2 + y^2)/2]$ , i.e., the parallel component  $\Theta_{\parallel}$  represents the difference between  $z^2$  and the average  $(x^2 + y^2)/2$  of the in-plane ( $xy$ ) moments. It therefore seems reasonable to consider  $(x^2 - y^2)$  as a measure of the CDD anisotropy in the  $xy$  plane. The quadrupole anisotropy  $\delta\Theta_{\Pi}$  is defined as  $\delta\Theta_{\Pi} = |(\Theta_{xx} - \Theta_{yy})|$ , which in terms of Cartesian moments becomes  $\delta\Theta_{\Pi} = (3/2)|(x^2 - y^2)|$ . Most importantly, from Tables II–IV, it follows that  $\delta\Theta_{\Pi}$  is proportional to the irreducible component  $\Theta_2^{(2)} \propto [(x^2 - y^2)/2]$ , that is,  $\delta\Theta_{\Pi}$  has a defined symmetry character—it transforms like the real part ( $A_1, C_{2v}$ ) of the  $\Delta$  representation of the  $C_{\infty v}$  point group.

Summarizing, Cartesian  $\Theta_{ij}$ 's are described by the following: (a)  $n=1$  parameter for  $\Sigma, \Delta, \Phi, \dots$ , for which it holds that  $\Theta_{zz}[P_0^{(2)}] = -2\Theta_{xx} = -2\Theta_{yy} \equiv (z^2 - x^2)$ ; but (b)  $n=2$  parameters for  $\Pi$  states,  $\Theta_{zz} = [z^2 - (x^2 + y^2)/2]$  and  $\delta\Theta_{\Pi}[P_2^{(2)}] = (3/2)|(x^2 - y^2)|$ . Both perpendicular moments,  $\Theta_{xx} = -(\Theta_{zz} + \delta\Theta_{\Pi})/2$ , and  $\Theta_{yy} = -(\Theta_{zz} - \delta\Theta_{\Pi})/2$ , are equidistantly placed above and below a reference value of  $-\Theta_{zz}/2$ .

Hirschfelder *et al.*<sup>19</sup> gave a similar definition of the quadrupole ( $Q_{ij}$ ) but with a factor *twice* that of Buckingham's,<sup>3</sup> e.g., their  $Q_{zz} = [2z^2 - (x^2 + y^2)]$  has to be compared with  $\Theta_{zz} = [z^2 - (x^2 + y^2)/2]$  from Ref. 3. Caution is in order when comparing literature data: experimentalists generally report  $Q_{ij}$ 's whereas theoreticians favor  $\Theta_{ij}$ 's. Expressions for the components  $Q_{zz}$ ,  $Q_{xx}$ , and  $Q_{yy}$  as a function of irreducible terms  $Q_m^{(l)}$  (twice our  $P_m^{(l)}$ ) were derived by Hirschfelder *et al.*,<sup>19</sup> which reported *two* independent values:  $Q_{zz} = 2Q_{(2)}^0$  and  $\delta Q = (Q_{(2)}^2 + Q_{(2)}^{-2})/2$ —the latter equivalent to  $\delta\Theta_{\Pi}$ ; the  $Q_{xx}$  and  $Q_{yy}$  components are  $(-Q_{zz} \pm \delta Q)/2$ . These old expressions have been overlooked in practically all theoretical studies dealing with the quadrupole moment of  $\Pi$  states.

**Octopole moment.** Only three Cartesian moments are nonzero ( $z^3, x^2z, y^2z$ ). The traceless octopole  $\Omega_{iiz}$  ( $i=x, y, z$ )

TABLE V. Cartesian components  $\Phi_{ijij}$  of the traceless hexadecapole moment  $\Phi$  of linear ( $C_{\infty v}$ ) molecules in terms of fourth-electric moments. The real parts of the nonzero irreducible components  $\Phi_0^{(4)}$ ,  $\Phi_{|2|}^{(4)}$ , and  $\Phi_{|4|}^{(4)}$  are given in footnote a.

Hexadecapole <sup>a-d</sup>	zzzz ( $z^4$ )	xxxx ( $x^4$ )	yyyy ( $y^4$ )	xxzz ( $x^2z^2$ )	yyzz ( $y^2z^2$ )	xyxy ( $x^2y^2$ )
$\Phi_{zzzz}$ ( $Z^4$ )	1	3/8	3/8	-3	-3	6/8
$\Phi_{xxxx}$ ( $X^4$ )	3/8	1	3/8	-3	6/8	-3
$\Phi_{yyyy}$ ( $Y^4$ )	3/8	3/8	1	6/8	-3	-3
$\Phi_{xxzz}$ ( $X^2Z^2$ )	-1/2	-1/2	1/8	27/8	-3/8	-3/8
$\Phi_{yyzz}$ ( $Y^2Z^2$ )	-1/2	1/8	-1/2	-3/8	27/8	-3/8
$\Phi_{xyxy}$ ( $X^2Y^2$ )	1/8	-1/2	-1/2	-3/8	-3/8	27/8

<sup>a</sup> $\Phi_0^{(4)} \propto [3(x^4+y^4)/4 - 6(x^2z^2+y^2z^2) + (3/2)x^2y^2 + 2z^4]$ ;  $\Phi_{|2|}^{(4)} \propto [(x^4-y^4)/4 - (3/2)(x^2z^2-y^2z^2)]$ ;  $\Phi_{|4|}^{(4)} \propto [(x^4+y^4)/4 - (3/2)x^2y^2]$ .

<sup>b</sup>For example,  $\Phi_{zzzz}$  is given by the expansion  $[1z^4 + (3/8)(x^4+y^4) - 3(x^2z^2+y^2z^2) + (6/8)x^2y^2]$ .

<sup>c</sup>Traceless conditions:  $\Phi_{zzzz} = -(\Phi_{xxzz} + \Phi_{yyzz})$ ,  $\Phi_{xxxx} = -(\Phi_{xxzz} + \Phi_{xyxy})$ , and  $\Phi_{yyyy} = -(\Phi_{yyzz} + \Phi_{xyxy})$ . Equivalently,  $(\Phi_{zzzz} + \Phi_{xxxx} + \Phi_{yyyy}) = -2(\Phi_{xxzz} + \Phi_{yyzz} + \Phi_{xyxy}) = (7/4)[(z^4 + x^4 + y^4) - 3(x^2z^2 + y^2z^2 + x^2y^2)]$ .

<sup>d</sup>Anisotropies: (i)  $\delta\Phi_{\Pi} \propto \Phi_{|2|}^{(4)} = |\Phi_{xxxx} - \Phi_{yyyy}| = |\Phi_{xxzz} - \Phi_{yyzz}| = (5/8)[(x^4 - y^4) - 6(x^2z^2 - y^2z^2)]$ . Only  $\Pi$  states have  $\delta\Phi_{\Pi} \neq 0$ . (ii)  $\delta\Phi_{\Delta} \propto \Phi_{|4|}^{(4)} = (1/7)|\Phi_{xxxx} + \Phi_{yyyy} - 6\Phi_{xyxy}| = (5/8)[(x^4 + y^4) - 6(x^2y^2)]$ . Only  $\Delta$  states have  $\delta\Phi_{\Delta} \neq 0$ .

is structurally closely related to the quadrupole  $\Theta_{ii}$ , as seen by comparing their parallel components,  $\Omega_{zzz} = z[z^2 - 3(x^2 + y^2)/2]$  vs  $\Theta_{zz} = [z^2 - (x^2 + y^2)/2]$ . When  $x^2z = y^2z$  (axial symmetry), it can be written as  $\Omega_{zzz} = (z^3 - 3x^2z)$ , where the moment  $z^3$  is being compared with three times the mixed component  $x^2z$ ; it also holds  $\Omega_{xxz} = \Omega_{yyz} = -\Omega_{zzz}/2 = -(z^3 - 3x^2z)/2$ .

We define the  $\Pi$ -type octopole anisotropy as  $\delta\Omega_{\Pi} = |\Omega_{xxz} - \Omega_{yyz}| = (5/2)|x^2z - y^2z|$ , which is nonzero if  $x^2z \neq y^2z$ , and therefore only satisfied by  $\Pi$  states (Appendix A). According to Table II,  $\delta\Omega_{\Pi}$  transforms like the irreducible component  $P_{|m|=2}^{(3)} [= \Omega_2^{(3)}]$  of  $\Delta/A_1$  character (as does  $\delta\Theta_{\Pi}$ ). These features parallel those noted for the quadrupole, i.e., Cartesian components are fully described as followed: (a) by  $n=1$  independent parameter  $\Omega_{zzz} = -2\Omega_{xxz} = -2\Omega_{yyz}$  [ $\equiv (z^2 - 3x^2z)$ ] in  $\Sigma, \Delta, \Phi, \dots$  states; but (b) by  $n=2$  free parameters in  $\Pi$  states, i.e.,  $\Omega_{zzz} = [z^3 - 3(x^2z + y^2z)/2]$  and  $\delta\Omega_{\Pi}$ . Here, one perpendicular  $\Omega$  component is given by  $-(\Omega_{zzz} + \delta\Omega_{\Pi})/2$ , and the other by  $-(\Omega_{zzz} - \delta\Omega_{\Pi})/2$ , that is, they are symmetrically shifted up and down, by  $\delta\Omega_{\Pi}/2$ , relative to  $-\Omega_{zzz}/2$ .

**Hexadecapole moment.** Table V lists Cartesian hexadecapole  $\Phi_{ijij}$ 's as linear combinations of fourth-order moments [Eqs. (5d) and (5e)]. The numerical  $6 \times 6$  array in Table V can be divided in four  $3 \times 3$  quadrants, each symmetric along the diagonal. Contraction of a fourth-rank tensor gives three traceless conditions:  $(\Phi_{zzzz} + \Phi_{xxzz} + \Phi_{yyzz}) = 0$ ;  $(\Phi_{xxxx} + \Phi_{xyxy} + \Phi_{xxzz}) = 0$ ; and  $(\Phi_{yyyy} + \Phi_{yyzz} + \Phi_{xyxy}) = 0$ , or equivalently,  $(\Phi_{zzzz} + \Phi_{xxxx} + \Phi_{yyyy}) = -2(\Phi_{xxzz} + \Phi_{yyzz} + \Phi_{xyxy})$ , i.e., the sum of the first three rows in Table V is twice the sum of the lowest three ones, and of opposite sign. These relations between Cartesian  $\Phi_{ijij}$ 's are valid for any type of electronic state and/or molecular symmetry.

Additional constraints on the  $\Phi_{ijij}$ 's arise when the fourth moments  $x^4, y^4, x^2y^2$ , etc., follow certain relationships among themselves due to the (rotational) symmetry of the given state (see Appendix A). For example, consider the contribution of  $x^4$  and  $y^4$  to both  $\Phi_{xxxx}$  and  $\Phi_{yyyy}$ . As seen in Table V,  $\Phi_{xxxx} = x^4 + (3/8)y^4$ , and  $\Phi_{yyyy} = (3/8)x^4 + y^4$ , that is,

both components differ by a simple exchange of coefficients (1 vs 3/8). A similar situation holds for  $\Phi_{xxxx}$  and  $\Phi_{yyyy}$  with respect to  $x^2z^2$  and  $y^2z^2$  (-3 vs 6/8). Other fourth moments,  $z^4$  and  $x^2y^2$ , contribute equally to  $\Phi_{xxxx}$  and  $\Phi_{yyyy}$  (3/8 and -3). Thus, if the equality  $\Phi_{xxxx} = \Phi_{yyyy}$  is valid, the conditions  $x^4 = y^4$  and  $x^2z^2 = y^2z^2$  are also true, and vice versa. Further,  $\Phi_{xxzz} = \Phi_{yyzz}$  is valid when the conditions  $x^4 = y^4$  and  $x^2z^2 = y^2z^2$  are fulfilled. Summarizing,  $\Phi_{xxxx} = \Phi_{yyyy}$  implies that  $\Phi_{xxzz} = \Phi_{yyzz}$  is also true. The same relations are satisfied by the Cartesian moments,  $(x^4 = y^4) \Leftrightarrow (x^2z^2 = y^2z^2)$ .

The components  $\Phi_{|m|}^{(4)} \equiv P_{|m|}^{(4)} (|m|=2, 4)$  of  $\Sigma$  states are such that  $\Phi_2^{(4)}$  and  $\Phi_4^{(4)}$  vanish. The condition  $\Phi_2^{(4)} = 0$  leads to the equalities  $\Phi_{xxxx} = \Phi_{yyyy}$  and  $\Phi_{xxzz} = \Phi_{yyzz}$ , while  $\Phi_4^{(4)} = 0$  determines the restrictions  $\Phi_{xyxy} = (1/3)\Phi_{xxxx} = (1/3)\Phi_{yyyy}$ . The six Cartesian  $\Phi_{ijij}$ 's of a  $\Sigma$  state are interrelated (taking  $\Phi_{zzzz} \equiv Z^4$  as reference, and defining  $\Phi_{xxxx} \equiv X^4$ ,  $\Phi_{xxzz} \equiv X^2Z^2$ , etc.) as follows:

$$Z^4 = 8X^2Y^2 = (8/3)X^4 = (8/3)Y^4 = -2X^2Z^2 = -2Y^2Z^2.$$

Clearly,  $\Sigma$  states have one independent  $\Phi$  component.<sup>5,6</sup> The relations between  $\Phi_{ijij}$ 's in  $\Pi$  and  $\Delta$  states ( $n=2$ ) are derived in Appendix A. The two independent parameters are the parallel component ( $\Phi_0^{(4)}$ ) and the anisotropy  $\delta\Phi_{\Pi}$  or  $\delta\Phi_{\Delta}$  (both defined in Sec. IV B).

## B. The $\Theta$ , $\Omega$ , and $\Phi$ moments calculated for diatomics in $\Sigma$ , $\Pi$ , $\Delta$ , and $\Phi$ states

The quadrupole to hexadecapole moments have been calculated for the  $2\Sigma^+$ ,  $2\Pi$ ,  $2\Delta$ ,  $3\Delta$ ,  $3\Phi$ , and  $4\Phi$  ground states of CN, NO, NiH, TiO, CoF, and TiF, respectively, as well as on the  $a^3\Pi_u$  excited state of  $C_2$ . Our results are meant to exemplify the topics discussed here, rather than to set benchmark values. As is well known,<sup>33</sup> accurate calculations of  $2^l$  poles require extended basis sets containing long-range atomic orbitals and reliable methods for evaluating wave functions.

The data are obtained with GAUSSIAN03,<sup>34</sup> at the B3LYP/aug-cc-pVQZ level for CN, NO,  $C_2$ , and with



TABLE VI. Second and third Cartesian ( $r_{\alpha}r_{\beta}$ ,  $r_{\alpha}r_{\beta}r_{\gamma}$ ), quadrupole, and octopole moments ( $\Theta_{zz}$ ,  $\Omega_{zzz}$ ) for radical with  $^2\Sigma^+$ ,  $^2\Pi$ ,  $^{2,3}\Delta$ , and  $^{3,4}\Phi$  ground states. Anisotropies ( $\delta\Theta_{\Pi}$ ,  $\delta\Omega_{\Pi}$ ) are also given. Data in D Å for  $r_{\alpha}r_{\beta}$ ,  $\Theta_{zz}$ , and  $\delta\Theta_{\Pi}$ ; in D Å<sup>2</sup> for  $r_{\alpha}r_{\beta}r_{\gamma}$ ,  $\Omega_{zzz}$ , and  $\delta\Omega_{\Pi}$ . Conversion factors 1 a.u.=1.3449 D Å for  $\Theta$ , and 1 a.u.=0.7117 D Å<sup>2</sup> for  $\Omega$ . Bond distances (Å, expt.: 1.1718 (CN), 1.1508 (NO), 1.3119 (C<sub>2</sub>), 1.4756 (NiH), and 1.61 (TiO) (Ref. 35); 1.762, est. (CoF) [Ref. 36(a)] [close to 1.738, new] [Ref. 36(b)]; and 1.8311 (TiF) (Ref. 37).

		$-zz$ ( $z^2$ )	$-xx$ ( $x^2$ )	$-yy$ ( $y^2$ )	$\Theta_{zz}$ <sup>a</sup>	$\delta\Theta_{\Pi}$ <sup>b</sup>
CN	( $X^2\Sigma^+$ )	10.489	11.083	11.083	0.594	0
NO	( $X^2\Pi$ )	11.477	9.734	10.860	-1.180	1.689
CC	( $a^3\Pi_u$ )	12.341	12.682	10.745	-0.628	2.906
NiH	( $X^2\Delta$ )	16.494	15.227	15.227	-1.267	0
TiO	( $X^3\Delta$ )	25.960	22.256	22.256	-3.704	0
CoF	( $X^3\Phi$ )	26.634	19.374	19.374	-7.260	0
TiF	( $X^4\Phi$ )	30.294	21.638	21.638	-8.656	0
		$-zzz$ ( $z^3$ )	$-xxz$ ( $x^2z$ )	$-yyz$ ( $y^2z$ )	$\Omega_{zzz}$ <sup>c</sup>	$\delta\Omega_{\Pi}$ <sup>d</sup>
CN	( $X^2\Sigma^+$ )	0.164	-0.177	-0.177	-0.695	0
NO	( $X^2\Pi$ )	-2.808	-0.506	-0.962	0.606	1.140
NiH	( $X^2\Delta$ )	-12.847	-3.372	-3.372	2.731	0
TiO	( $X^3\Delta$ )	-0.088	1.419	1.419	4.345	0
CoF	( $X^3\Phi$ )	-0.411	1.464	1.464	4.803	0
TiF	( $X^4\Phi$ )	13.820	5.955	5.955	4.045	0

<sup>a</sup>CN:  $\Theta_{zz}$ =0.849 (HF, theor.) (Ref. 39); NO, literature  $\Theta$ 's (I) *experimental* (Ref. 13),  $\langle\Theta\rangle\approx 2.4$  (Hirschfelder's definition) (Ref. 19) or  $\langle\Theta\rangle\approx 1.2$  (Buckingham's) (Ref. 3); and (II) *theoretical*: -0.913 (CI) [Ref. 38(a)], -0.973 (CI) [Ref. 38(b)], -1.122 (CI) [Ref. 38(c)] and -1.114 (MRDCI/B<sub>k</sub>) (Ref. 8).

<sup>b</sup>Anisotropy  $\delta\Theta_{\Pi}=|\Theta_{xx}-\Theta_{yy}|=(3/2)|(x^2-y^2)|$ . It holds that  $\delta\Theta_{\Pi}\neq 0$  only if  $x^2\neq y^2$  ( $\Pi$  states). Cartesian components:  $\Theta_{xx}=(-\Theta_{zz}+\delta\Theta_{\Pi})/2$ ; and  $\Theta_{yy}=(-\Theta_{zz}-\delta\Theta_{\Pi})/2$ .

<sup>c</sup>CN:  $\Omega_{zzz}=-1.499$  D Å<sup>2</sup> (Hartree-Fock) (Ref. 39);  $\Omega\equiv 0$  for homonuclear ( $D_{\infty h}$ ) molecules such as C<sub>2</sub>.

<sup>d</sup>Anisotropy  $\delta\Omega_{\Pi}=|\Omega_{xxz}-\Omega_{yyz}|=(5/2)|(x^2z-y^2z)|$ . It holds that  $\delta\Omega_{\Pi}\neq 0$  only if  $x^2z\neq y^2z$  ( $\Pi$  states). Cartesian components:  $\Omega_{xxz}=(-\Omega_{zzz}+\delta\Omega_{\Pi})/2$ ; and  $\Omega_{yyz}=(-\Omega_{zzz}-\delta\Omega_{\Pi})/2$ .

B3LYP/6-311+G(2df) for TiO. The NiH, CoF, and TiF radicals are studied at the complete active space self-consistent field level (B3LYP gives “mixed” structures: Cartesian moments which should vanish by symmetry are non-zero.) The bond distances are given in Table VI.<sup>35–37</sup> All multipoles considered for our selection of molecules are origin dependent (except for the C<sub>2</sub> quadrupole moment); here we report the G03 data calculated with respect to the center of positive charges.

Cartesian moments, parallel components

( $\Theta_{zz}$ ,  $\Omega_{zzz}$ ,  $\Phi_{zzzz}$ ), and anisotropies ( $\delta\Theta_{\Pi}$ ,  $\delta\Omega_{\Pi}$ ,  $\delta\Phi_{\Pi}$ ,  $\delta\Phi_{\Delta}$ ) are listed in Tables VI and VII. According to Table VI, the pairs of Cartesian moments ( $x^2, y^2$ ) and ( $x^2z, y^2z$ ) are equal for  $\Sigma^+$ ,  $\Delta$ , and  $\Phi$  but different for  $\Pi$ . As discussed in Sec. III,  $\Pi$  states are the only ones having anisotropic second and third moments (nonzero  $\delta\Theta_{\Pi}$ ,  $\delta\Omega_{\Pi}$ , i.e.,  $n=2$  parameters are needed to describe  $\Theta$  and  $\Omega$ ). By contrast, the Cartesian moments of  $\Delta$  and  $\Phi$  states are such that  $x^2=y^2$  and  $x^2z=y^2z$ —they behave like the axially symmetric  $\Sigma$  ( $n=1$ ) states.

TABLE VII. Fourth-order Cartesian electric moments, hexadecapole moment component  $\Omega_{zzzz}$ , and anisotropies  $\delta\Phi_{\Pi}$ ,  $\delta\Phi_{\Delta}$  for selected diatomic radicals of  $^2\Sigma^+$ ,  $^2,3\Pi$ ,  $^{2,3}\Delta$ , and  $^{3,4}\Phi$  character. All data in D Å<sup>3</sup>. Calculated using expansions from Table V and geometries from Table VI. Conversion factor: 1 a.u.=0.3766 D Å<sup>3</sup>.

		$-zzzz$ ( $z^4$ )	$-xxxx$ ( $x^4$ )	$-yyyy$ ( $y^4$ )	$-xxzz$ ( $x^2z^2$ )	$-yyzz$ ( $y^2z^2$ )	$-xxyy$ ( $x^2y^2$ )	$\Phi_{zzzz}$ <sup>a</sup>	$\delta\Phi_{\Pi}$ <sup>b</sup>	$\delta\Phi_{\Delta}$ <sup>c</sup>
CN	( $X^2\Sigma^+$ )	33.994	11.652	11.652	7.450	7.450	3.884	-0.946 <sup>d</sup>	0	0
NO	( $X^2\Pi$ )	31.788	7.827	9.732	6.225	7.434	2.927	0.409	3.343	0
CC	( $a^3\Pi_u$ )	48.003	16.453	12.140	10.561	9.393	4.768	4.713	1.684	0
NiH	( $X^2\Delta$ )	43.364	22.001	22.001	10.694	10.694	7.535	-1.352	0	0.755
TiO	( $X^3\Delta$ )	124.977	41.546	41.546	27.588	27.588	14.715	-1.645	0	3.249
CoF	( $X^3\Phi$ )	131.533	27.964	27.964	25.630	25.630	9.321	-5.717	0	0
TiF	( $X^4\Phi$ )	172.578	42.749	42.749	35.166	35.166	14.250	-4.331	0	0

<sup>a</sup>Jansen (Ref. 4) axial symmetry,  $\Phi'_{zzzz}=[(z^4+x^4)-6x^2z^2]\equiv[(z^4+y^4)-6y^2z^2]$ . Our data support  $\Phi'_{zzzz}=\Phi_{zzzz}$  (Table V expansion) for the symmetries  $\Sigma$  and  $\Phi$  but not for  $\Pi$  or  $\Delta$ .

<sup>b</sup>Anisotropy  $\delta\Phi_{\Pi}\{\propto\Phi_{[2]}^{(4)}\}=|\Phi_{xxxx}-\Phi_{yyyy}|=|\Phi_{xxzz}-\Phi_{yyzz}|=(5/8)|(x^4-y^4)-6(x^2z^2-y^2z^2)|$ . Only  $\Pi$  states have  $\delta\Phi_{\Pi}\neq 0$ .

<sup>c</sup>Anisotropy  $\delta\Phi_{\Delta}\{\propto\Phi_{[4]}^{(4)}\}=(1/7)|\Phi_{xxxx}+\Phi_{yyyy}-6\Phi_{xxyy}|=(35/8)|(x^4+y^4)-6(x^2y^2)|$ . Only  $\Delta$  states have  $\delta\Phi_{\Delta}\neq 0$ .

<sup>d</sup>CN:  $\Phi_{zzzz}=-1.898$  D Å<sup>3</sup> (Hartree-Fock) (Ref. 39).

As seen in Table VII, the fourth-order Cartesian moments are such that  $x^4=y^4$  and  $x^2z^2=y^2z^2$  for all but  $\Pi$  states. We define the hexadecapole  $\Pi$ -type anisotropy as  $\delta\Phi_{\Pi}=|(\Phi_{xxxx}-\Phi_{yyyy})|=(\Phi_{xxzz}-\Phi_{yyzz})$ , which according to Table V, reads as  $\delta\Phi_{\Pi}=(5/8)|(x^4-y^4)-6(x^2z^2-y^2z^2)|$ . Note that (i)  $\delta\Phi_{\Pi}\neq 0$  only for  $\Pi$  states; and (ii)  $\delta\Phi_{\Pi}$  is proportional to  $\text{Re}[\Phi_{\pm 2}^{(4)}]$ , Tables II and V; and (iii)  $\delta\Phi_{\Pi}$  is of  $A_1/\Delta$  symmetry ( $C_{2v}/C_{\infty v}$ ), like  $\delta\Phi_{\Pi}$  and  $\delta\Phi_{\Pi}$ . The  $\Phi$  moment also has a second anisotropy, of  $\Delta$  type, defined as  $\delta\Phi_{\Delta}=(1/7)|(\Phi_{xxxx}+\Phi_{yyyy})-6\Phi_{xxzz}|=(5/8)|(x^4+y^4)-6(x^2y^2)|$ , which is proportional to  $\text{Re}[\Phi_{\pm 4}^{(4)}]$ . Most importantly,  $\delta\Phi_{\Delta}$  behaves like the  $A_1/\Gamma$  representation in  $C_{2v}/C_{\infty v}$  symmetry. Note that  $\delta\Phi_{\Delta}\neq 0$  only for  $\Delta$  states—as found for NiH and TiO (Table VII).

To the best of our knowledge, previous multipole data on these radicals are limited to  $\Theta$  of  $\text{NO}(X^2\Pi)$ —experiment and theory—and  $\Theta$ ,  $\Omega$ , and  $\Phi$  of  $\text{CN}(X^2\Sigma^+)$ —theory. For NO (gas phase), the experimental  $|\Theta|$ 's range from 0.80 to 3.04 D Å,<sup>5,13</sup> with one paper recommending  $-1.8$  D Å,<sup>5</sup> and another 2.4 D Å.<sup>13</sup> Unsatisfactory remain as well three aspects of the experimental data: (i) what definition of the  $\Theta$  moment was used (Sec. IV A); (ii) what is the relation between the measured  $\Theta$ 's and the components  $\Theta_{xx}\neq\Theta_{yy}\neq\Theta_{zz}$ ; and (iii) which is the sign of  $\Theta_{zz}$ . Theoretical configuration interaction (CI) studies reported  $\Theta_{zz}$ 's from  $-0.913$  to  $-1.122$  D Å (Table VI),<sup>8,38</sup> but none of them listed  $(\Theta_{xx}-\Theta_{yy})$ . Our  $\Theta_{zz}=-1.175$  D Å agree with them, all supporting  $\Theta_{zz}<0$ . Buckingham's quadrupole<sup>3</sup> was used in all calculations, so that a factor of 2 deviation relative to  $\Theta(\text{expt.})\approx 2.4$  D Å could be explained if experimentalists had employed the definition of Hirschfelder *et al.*<sup>19</sup>

Taking  $\Theta_{zz}=-1.12$  D Å as a best estimate, we would like to mention that neglecting the anisotropy  $\delta\Theta_{\Phi}$  in NO leads to 0.56 D Å for both  $\Theta_{xx}$  and  $\Theta_{yy}$ . However, using  $\delta\Theta_{\Pi}\approx 1.7$  D Å (Table VI), it follows that  $\Theta_{xx}\approx 1.41$  and  $\Theta_{yy}\approx -0.29$  D Å, i.e., each component has little in common with an average value of 0.56 D Å. Clearly, the  $n=1$  rule fails completely for  $\Pi$  states.

The previous Hartree-Fock study on  $\text{CN}(X^2\Sigma^+)$  (Ref. 39) found 0.849 D Å for  $\Theta_{zz}$ ,  $-1.499$  D Å<sup>2</sup> for  $\Omega_{zzz}$ , and  $-1.898$  D Å<sup>3</sup> for  $\Phi_{zzzz}$ , to be compared with our density functional theory (DTF) results of 0.594,  $-0.695$ , and  $-0.946$  (same order and units). A QCISD/aug-cc-pVTZ calculation<sup>40</sup> finds 0.606 D Å for  $\Theta_{zz}$ ,  $-0.820$  D Å<sup>2</sup> for  $\Omega_{zzz}$ , and  $-1.179$  D Å<sup>3</sup> for  $\Phi_{zzzz}$ , in reasonable accord with the DFT data.

## V. SUMMARY AND CONCLUDING REMARKS

This work clarifies discrepancies in the literature about the number of free parameters ( $n$ ) needed to describe electric  $2^l$ -pole moments for linear states with  $\Lambda>0$ . Considering two representative states— $\Sigma$  vs  $\Pi$ —it is experimentally known that they have different  $n$ 's for a variety of second-rank properties: traceless hfcc's ( $T_{ij}, eQq_{ij}$ ) have  $n=1$  for  $\Sigma$  but  $n=2$  for  $\Pi$ , while a traced tensor ( $g$  factor) has  $n=2$  for  $\Sigma$  but  $n=3$  for  $\Pi$ .<sup>1,2,41</sup> With this information, the  $n$  value for the traceless quadrupole  $\Theta_{ij}$  is expected to be  $n=1$  for  $\Sigma$  and  $n=2$  for  $\Pi$ . This cannot be tested, however, since the entire

set  $\Theta_{xx}, \Theta_{yy}, \Theta_{zz}$  has not been measured for any  $\Pi$  radical. Contrastingly, theoretical papers<sup>3-8,25</sup> have assigned  $n=1$  to all possible  $2^l$  poles of every linear state—no connection between  $l$  and  $\Lambda$ . Thus, it seems that  $n=2$  for  $eQq_{ij}(\text{expt.})$  but  $n=1$  for  $\Theta_{ij}(\text{theor.})$ , in spite of both tensors having the same structure. Critical analysis of the literature unravels a common malaise: the recommended  $n$ 's had unwarily been derived assuming that the CDD of any linear state is axially symmetric: true for  $\Sigma$  but not for  $\Lambda\neq 0$  states. A fresh look is needed on the question of how to describe correctly multipoles in degenerate linear states.

To solve the problem, we investigated the relation between the rank  $l$  of electric  $2^l$  poles and the  $\Lambda$  value. We use irreducible representations  $P_m^{(l)}\propto r^l Y_m^l(\theta, \varphi)$  of the  $2^l$  poles.<sup>19,25,26</sup> As a result, a dependency has been established between  $n$  ( $=1$  or  $2$ ), the multipole rank  $l$  and the state quantum number  $\Lambda$ . The key relation is governed by a cut-off value of  $l=2|\Lambda|$ : All  $2^l$  poles of rank below  $2\Lambda$  have one free component, whereas those of rank  $l\geq 2\Lambda$  have two. Specifically, for  $\Pi$  states  $n=2$  components are needed for all  $2^l$  poles ( $l\geq 2$ ), namely,  $\Theta_{zz}$  and  $\delta\Theta_{\Pi}[\equiv P_2^{(2)}]$ ;  $\Omega_{zzz}$  and  $\delta\Omega_{\Pi}[\equiv P_2^{(2)}]$ ;  $\Phi_{zzzz}$  and  $\delta\Phi_{\Pi}[\equiv P_2^{(4)}]$ ;  $[P_0^{(l)}, P_2^{(l)}]$  for higher multipoles. Deviations from axial symmetry are noticeable starting with the hexadecapole ( $2^4$ ) for  $\Delta$ , and with the  $2^6$  pole for  $\Phi$ .

Another interesting finding is that  $\Lambda=2, 3, \dots$  (non- $\Pi$ ) states also require  $n=2$  components to describe  $2^p$  poles of rank  $p=2\Lambda$ , and higher  $2^l$  poles with  $l>p$ . They follow the  $n=1$  rule up to the  $2^{(p-1)}$  pole. Thus, the possible values of  $n$  for multipoles of rank 2–7 in  $C_{\infty v}$  molecules are as follows: (1) *Second* and *third* rank ( $\Theta_{ij}, \Omega_{ijk}$ ):  $n=2$  for one state symmetry ( $\Pi$ ), but  $n=1$  for  $\Sigma, \Delta, \Phi$ , etc.; (2) *fourth* ( $\Phi_{ijkl}$ ) and *fifth* rank:  $n=2$  for two state symmetries ( $\Pi, \Delta$ ), but  $n=1$  for  $\Sigma, \Phi, \Gamma$ , etc.; and (3) *sixth* and *seventh* rank:  $n=2$  for three state symmetries ( $\Pi, \Delta, \Phi$ ), but  $n=1$  for others— $\Sigma$  plus the more rare cases (what multipoles concern)  $\Gamma, H, I, \dots$ , ( $\Lambda=4, 5, 6, \dots$ ).

Not all rules apply to  $D_{\infty h}$  molecules:  $2^l$  poles with even  $l$  (quadrupole, hexadecapole) behave like  $C_{\infty v}$  but those with odd  $l$  (dipole, octopole) identically vanish for all states.

The “parallel” component ( $P_{\parallel}$ ) is always nonzero, while the second free component (i.e., when  $n=2$  applies) is taken by us to define the multipole anisotropy  $[\delta(P)_{2\Lambda}]$  in the  $xy$  plane. Expressions are derived for the first time for the Cartesian  $\Phi_{ijjj}$ 's of the hexadecapole moment in  $\Pi$  and  $\Delta$  states, with  $P_{\parallel}$  and  $\delta(P)_{\Lambda}$  as free parameters. Previous expressions<sup>5,6</sup> for  $\Sigma$  states are also valid for  $\Phi$  states. The multipole expansions of the charge density in linear states read as follows:

$$\Sigma(\Lambda=0) \text{ states} \Rightarrow \mathbf{F}\{\mu_z, \Theta_{zz}, \Omega_{zzz}, \Phi_{zzzz}, \xi_0^{(5)}, \dots, \xi_0^{(l)}, \dots\}, \quad (6a)$$

$$\begin{aligned} \Pi(\Lambda=1) \text{ states} \\ \Rightarrow \mathbf{F}\{\mu_z, [\Theta_{zz}, \delta\Theta_{\Pi}], [\Omega_{zzz}, \delta\Omega_{\Pi}], [\Phi_{zzzz}, \delta\Phi_{\Pi}], \dots, \\ [\xi_0^{(l)}, \xi_2^{(l)}]_{l\geq 2}, \dots\}, \end{aligned} \quad (6b)$$

TABLE VIII. Relations between the nonzero Cartesian fourth-electric moments  $x^4$ ,  $y^4$ ,  $x^2y^2$ ,  $x^2z^2$ , and  $y^2z^2$  for linear states ( $C_{\infty v}$ ) of  $\Sigma$ ,  $\Pi$ ,  $\Delta$ , and  $\Phi$  character.

State ( $\Lambda$ )	Relations			$\Phi_{zzzz}$ <sup>a</sup>	$\Phi_{zzzz}$ plus <sup>b</sup>
$\Sigma(0)$	$x^4=y^4$	$(x^4+y^4)=6(x^2y^2)^c$	$x^2z^2=y^2z^2$	$z^4+x^4-6x^2z^2$ <sup>d</sup>	$\cdots$ ( $n=1$ )
$\Pi(1)$	$x^4 \neq y^4$	$(x^4+y^4)=6(x^2y^2)^c$	$x^2z^2 \neq y^2z^2$	$z^4+(x^4+y^4)/2-3(x^2z^2+y^2z^2)$	$\delta\Phi_{\Pi}$ ( $n=2$ )
$\Delta(2)$	$x^4=y^4$	$(x^4+y^4) \neq 6(x^2y^2)^c$	$x^2z^2=y^2z^2$	$z^4+3(x^4+x^2y^2)/4-6x^2z^2$	$\delta\Phi_{\Delta}$ ( $n=2$ )
$\Phi(3)$	$x^4=y^4$	$(x^4+y^4)=6(x^2y^2)^c$	$x^2z^2=y^2z^2$	$z^4+x^4-6x^2z^2$ <sup>d</sup>	$\cdots$ ( $n=1$ )

<sup>a</sup> $\Phi_{zzzz}$  expansions by combining fourth-moment relationships (columns 2–4) with  $\Phi_{zzzz}$ , Table V.<sup>b</sup>Independent parameters ( $n$ ) for each state. See the text for details.<sup>c</sup>Compounded:  $x^4=y^4=3(x^2y^2)$ .<sup>d</sup>Reproduces Jensen's hexadecapole expansion for axially symmetric systems (Ref. 4).<sup>e</sup>Compounded:  $x^4=y^4 \neq 3(x^2y^2)$ . $\Delta(\Lambda=2)$  states

$$\Rightarrow \mathbf{F}\{\mu_z, \Theta_{zz}, \Omega_{zzz}, [\Phi_{zzzz}, \delta\Phi_{\Delta}], \dots, [\xi_0^{(l)}, \xi_4^{(l)}]_{l \geq 4}, \dots\}, \quad (6c)$$

 $\Phi(\Lambda=3)$  states

$$\Rightarrow \mathbf{F}\{\mu_z, \Theta_{zz}, \Omega_{zzz}, \Phi_{zzzz}, \dots, [\xi_0^{(l)}, \xi_6^{(l)}]_{l \geq 6}, \dots\}. \quad (6d)$$

Interestingly, the *higher* the  $\Lambda$  value ( $\geq 1$ ), the *smaller* the deviation from axial symmetry. The asymmetric nature of  $\Pi$ -CDD's can be seen by the ellipsoidal-shaped density contours for  $X^2\Pi$  of CH.<sup>42(a)</sup> Also, Ref. 42(b) shows cross sections of the  $(xy)$  anisotropies discussed here. Further, studies of collisions involving  $\Delta_g$  species [ $O_2(a^1\Delta_g)$ ] should include the  $\delta\Phi_{\Delta}$  anisotropy because of a shorter  $2^l$ -pole expansion in  $D_{\infty h}$  symmetry [ $\mathbf{F}\{\Theta_{zz}, \Phi_{zzzz}, \delta\Phi_{\Delta}, \dots, [\xi_0^{(l)}, \xi_4^{(l)}]_{l \geq 4}, \dots$  (even  $l\}$ ], as both  $\mu_z$  and  $\Omega_{zzz}$  moments vanish.

Calculations carried out for diatomics in  $\Sigma$ ,  $\Pi$ ,  $\Delta$ , and  $\Phi$  states confirm predictions made by our model. Although all non- $\Sigma$  states have axially asymmetric CDD's, our results show that  $\Pi$  states deviate at most from the symmetrical situation. This is in line with the experimental finding<sup>1,2</sup> that the hyperfine coupling constant  $d=(T_{xx}-T_{yy})$  is nonzero for  $\Pi$  but zero for  $\Delta$  states.

Now, an interesting question can be put forward: What other properties might also have been incorrectly treated regarding the value of  $n$  required for degenerate states? A brief literature search on dipole polarizabilities reveals that it has been stated, more frequently than not, that *two* components suffice to describe  $\Pi$  states— $\alpha_{zz}$  and  $\alpha_{xx}=\alpha_{yy}$ , or  $\beta_{zzz}$  and  $\beta_{xxz}=\beta_{yyz}$ . However, since  $\Pi$  states have *three* independent  $g$  factors,<sup>1,2,41</sup> one expects  $\alpha_{xx} \neq \alpha_{yy} \neq \alpha_{zz}$  and  $\beta_{xxz} \neq \beta_{yyz} \neq \beta_{zzz}$ .

According to the literature,<sup>6,26(c),43</sup> the second hyperpolarizability tensor  $\gamma_{ijkl}$  has *three* free parameters (a rule probably derived for an axially symmetric CDD), but clearly the  $\gamma$  partition for degenerate states should be different ( $n \approx 4$  or 5 for  $\gamma_{ijkl}$  in  $\Pi$  states).<sup>40</sup> Other properties probably needing careful reanalyses are oscillator strength sums,<sup>8,44</sup> NMR chemical shifts,<sup>45</sup> magnetizabilities,<sup>46</sup> Compton profiles,<sup>47</sup> polarizabilities other than of the dipole type, etc.<sup>3,6,43</sup>

The existence of a second nonzero independent multipole component in degenerate states is just one example of a more general picture characteristic of spatially degenerate states.<sup>48–50</sup> For a given operator  $P$ , there are two relevant

matrix elements, the diagonal  $\langle\Psi_{\Lambda}|P|\Psi_{\Lambda}\rangle$  and the off-diagonal  $\langle\Psi_{\Lambda}|P|\Psi_{-\Lambda}\rangle$ . The first case, where both  $\Lambda$ 's are of the same sign, applies to all states. However, under which conditions the “mixed” term  $\langle\Psi_{\Lambda}|P|\Psi_{-\Lambda}\rangle$  is nonzero depends on the operator  $P$ . Similar diagonal and off-diagonal couplings between two components in electronically degenerate states, not necessarily linear, are responsible for the Renner-Teller and Jahn-Teller splittings in linear and nonlinear, high-symmetry molecules.<sup>49(d),49(e)</sup> Other effects resulting from the coupling between  $+\Lambda$  and  $-\Lambda$  components are manifested in the  $\Lambda$ -doubling parameters  $p$  and  $q$  and on the existence of two different *perpendicular* electron-spin  $g_l$  and  $g_l'$  factors in  $^2\Pi$  states,<sup>1,2</sup> as recently investigated for  $X^2\Pi$  of  $FH^+$ ,  $ClH^+$ ,  $BrH^+$ ,<sup>41</sup> and  $A^2\Pi_u$  of  $N_2^+$ .<sup>51</sup>

Finally, we like to stress that one major motivation of this work has been to clarify a frequent *misconception* in the theoretical literature: that *axially symmetric charge densities* and *linear molecules*—the latter in *any* electronic state—are interchangeable concepts. Such a connection is strictly valid only for  $\Sigma$  states.

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## APPENDIX A: RELATIONS BETWEEN CARTESIAN COMPONENTS $\Phi_{ijjj}$ OF THE HEXADECAPOLE MOMENT $\Phi$ IN $\Sigma$ , $\Pi$ , $\Delta$ , AND $\Phi$ ELECTRONIC STATES

Below we present relationships between Cartesian components  $\Phi_{ijjj}$  ( $ii, jj=xx, yy, zz$ ) for the novel situation  $n=2$  in  $\Pi$  and  $\Delta$  states. The  $\Phi_{ijjj}$ 's obey the constraint ( $\Phi_{zzzz} + \Phi_{xxxx} + \Phi_{yyyy} = -2(\Phi_{xxzz} + \Phi_{yyzz} + \Phi_{xxyy})$ , which holds for all  $\Lambda$ 's. For simplicity, we label  $\Phi_{zzzz}=Z^4$ ,  $\Phi_{xxzz}=X^2Z^2$ , etc., so that  $(Z^4+X^4+Y^4)=-2(X^2Z^2+Y^2Z^2+X^2Y^2)$ . Other constraints among  $\Phi_{ijjj}$ 's can be established by considering how fourth-order moments are interrelated as dictated by  $\Phi_2^{(4)} \propto [e^{\pm 2i\varphi}]$  and  $\Phi_4^{(4)} \propto [e^{\pm 2i\varphi}]^2$  (Table II). Relationships among fourth-rank Cartesian moments are given in Table VIII.

Axial symmetry implies all  $2^l$ -pole components are  $\varphi$  independent, i.e.,  $\delta\Phi_{\Pi}[\Phi_2^{(4)}]=(7z^2-r^2)(x \pm iy)^2=0$ , and  $\delta\Phi_{\Delta}[\Phi_4^{(4)}]=(x \pm iy)^4=0$ . Expanding the real parts in Cartesian moments, axial symmetry imposes the conditions  $x^4=y^4$



$=3(x^2y^2)$ , and  $x^2z^2=y^2z^2$ . Altogether, for the  $\Phi_{ijj}$ 's of  $\Sigma$  and  $\Phi$  ( $n=1$ ) one obtains  $Z^4=8X^2Y^2=(8/3)X^4=(8/3)Y^4=-2X^2Z^2=-2Y^2Z^2$ .

For  $\Pi(\Delta)$  states, the  $\Phi_{ijj}$ 's are divided into two subsets. Adapting the  $\Phi_{ijj}$ 's in Table V by the  $\Pi$  constraints [ $x^4 \neq y^4$ ,  $(x^4+y^4)=6(x^2y^2)$  and  $x^2z^2 \neq y^2z^2$ ], Table VIII], the  $\Phi_{ijj}$ 's of a  $\Pi$  state can be expressed in terms of  $Z^4$  and  $\delta\Pi \equiv \delta\Phi_{\Pi}/2$ , namely, (a)  $X^2Y^2=(1/8)Z^4$ ; and (b)  $X^4=[(3/8)Z^4 + \delta\Pi]$ ;  $Y^4=[(3/8)Z^4 - \delta\Pi]$ ;  $X^2Z^2=[-(1/2)Z^4 + \delta\Pi]$ ;  $Y^2Z^2=[-(1/2)Z^4 - \delta\Pi]$ . Here, case (a) is anisotropy independent, while all relations in (b) depend on *two* parameters,  $Z^4$  and  $\delta\Pi$ .

For  $\Delta$  states, we combine the following: (i) the relations among Cartesian moments [ $x^4=y^4$ ;  $(x^4+y^4) \neq 6(x^2y^2)$ ; and  $x^2z^2=y^2z^2$  (Table VIII)]; and (ii) the anisotropy  $\delta\Phi_{\Delta}[\propto\Phi_{\Delta}^{(4)}]$ , defined as  $\delta\Phi_{\Delta}=(1/7)|(X^4+Y^4)-6X^2Y^2| \equiv (2/7)|X^4-3X^2Y^2| \equiv (5/4)|x^4-3x^2y^2|$ . The final relations for  $\Delta$  are as follows: (a)  $X^2Z^2=Y^2Z^2=-(1/2)Z^4$ ; and (b)  $X^4=Y^4=[(3/8)Z^4 + \delta\Delta]$ ;  $X^2Y^2=[(1/8)Z^4 - \delta\Delta]$ , and where  $\delta\Delta$  stands for  $\delta\Delta=(7/8)(\delta\Phi_{\Delta})$ .

## APPENDIX B: RELATIONS BETWEEN ELECTRONIC STATE QUANTUM NUMBER $\Lambda$ AND BOTH THE RANK $l$ AND $m$ COMPONENT OF THE IRREDUCIBLE CARTESIAN TENSOR $P_m^{(l)}$

The expectation value of a tensor component  $P_m^{(l)}(r, \theta, \varphi)$  for a  $\Lambda$  state  $\Psi_{\Lambda}(r, \theta, \varphi)$  is given by a matrix element (ME)  $\equiv \langle \Psi_{\Lambda'}(r, \theta, \varphi) | P_m^{(l)}(r, \theta, \varphi) | \Psi_{\Lambda}(r, \theta, \varphi) \rangle$ , which can be decomposed as  $\text{ME} \equiv \langle \underline{\Psi}_{\Lambda'} | \underline{P}_m^{(l)} | \underline{\Psi}_{\Lambda} \rangle \times \langle e^{i\Lambda'\varphi} | e^{im\varphi} | e^{i\Lambda\varphi} \rangle$  using the definitions  $\underline{\Psi}_{\Lambda}(r, \theta, \varphi) = \underline{\Psi}_{\Lambda}(r, \theta) e^{i\Lambda\varphi} \equiv \underline{\Psi}_{\Lambda} e^{i\Lambda\varphi}$ , and  $\underline{P}_m^{(l)}(r, \theta, \varphi) = \underline{P}_m^{(l)}(r, \theta) e^{im\varphi} \equiv \underline{P}_m^{(l)} e^{im\varphi}$ . Note that underlined terms depend on  $(r, \theta)$  only, while  $\Lambda' = -|\Lambda|$  and  $\Lambda = +|\Lambda|$ . For ME to be nonzero, *both*  $\langle \underline{\Psi}_{\Lambda'} | \underline{P}_m^{(l)} | \underline{\Psi}_{\Lambda} \rangle$  and  $\langle e^{i\Lambda'\varphi} | e^{im\varphi} | e^{i\Lambda\varphi} \rangle$  have to be nonzero. Integrating over  $\varphi$ ,  $\text{ME}(\varphi) = \langle e^{i\Lambda'\varphi} | e^{im\varphi} | e^{i\Lambda\varphi} \rangle = \int e^{i[m-(\Lambda'-\Lambda)]\varphi} d\varphi$  vanishes unless the condition  $m=(\Lambda'-\Lambda)$  is fulfilled. Possible cases are as follows: (i)  $m=0$ , that is, both  $\Lambda'$  and  $\Lambda$  are of the same sign. Actually, this diagonal term is independent of  $\Lambda$ , and therefore obeyed by any linear state; and (ii)  $m = \pm 2|\Lambda|$ , i.e.,  $\Lambda'$  and  $\Lambda$  are of opposite sign (off-diagonal ME). Working with real operators/wave functions, this condition reads  $|m|=2\Lambda$ —only *even*  $m$ 's are relevant. Thus, the “second” multipole component is  $|m|=2$  for  $\Pi$ ;  $|m|=4$  for  $\Delta$ ;  $|m|=6$  for  $\Phi$ ; and so forth.<sup>48–50</sup>

Any  $2^l$  pole ( $l \geq 1$ ) has a nonzero term,  $|m|=0$ , the parallel component. Since the maximum  $|m|$  value is  $l$ , the rule  $|m|=2\Lambda$  can be applied to a given  $\Lambda$  state only if the multipole rank  $l$  is such that it contains  $|m|=2\Lambda$ , or equivalently, if  $l \geq 2\Lambda$ . Important cases are as follows: (i)  $\Pi(\Lambda=1)$  states: a component of type  $|m|=2$  is found in  $\Theta_2^{(2)}, \Omega_2^{(3)}, \Phi_2^{(4)}, \dots, P_2^{(l)}$  (ii)  $\Delta(\Lambda=2)$  states: a  $|m|=4$  component only exists if  $l \geq 4$ , so that the hexadecapole is the lowest multipole revealing the CDD asymmetry in  $\Delta$  states; and (iii)  $\Phi(\Lambda=3)$  states: a  $|m|=6$  component only exists if  $l \geq 6$ , that is, none of the lower multipoles from  $l=2$  to  $l=5$  will detect the CDD asymmetry in  $\Phi$  states.

Regarding  $\langle \Psi_{\Lambda'} | \underline{P}_m^{(l)} | \Psi_{\Lambda} \rangle$ , the symmetry conditions under which this matrix element vanishes or not are those discussed in Sec. III B.

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