A nomenclature for Λ-doublet levels in rotating linear molecules

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It is proposed that the two Λ-doublet levels of linear molecules with nonzero electronic orbital angular momentum be labeled $\Lambda(A')$ and $\Lambda(A'')$, e.g., $\Pi(A')$ and $\Pi(A'')$ for Π states, etc., according to the following prescription: All series of levels in which the electronic wave function at *high J* is symmetric with reflection of the spatial coordinates of the electrons in the plane of rotation will be designated $\Lambda(A')$ for all values of J, and all those for which the electronic wave function is antisymmetric with respect to reflection will be denoted $\Lambda(A'')$. It is emphasized that this notation is meant to supplement, *and not replace*, the accepted spectroscopic e/f labeling and the parity quantum number. The utility of the $\Lambda(A')/\Lambda(A'')$ notation is that it is of most relevance in the mechanistic interpretation of reactive or photodissociative processes involving open-shell molecules.

I. INTRODUCTION

In diatomic molecular electronic states with $\Lambda \geqslant 1$, each rotational level is split into a closely spaced Λ doublet, which corresponds to linear combinations of the $+\Lambda$ and $-\Lambda$ projections of the electronic orbital angular momentum.[1] More generally, this pairing of closely spaced levels occurs in any linear molecule with a nonzero projection of angular momentum (electronic or vibrational) along the symmetry axis. The relative populations of the Λ-doublet levels in Π-state products have been measured for a number of reactions and photodissociation processes, as well as in gas–surface collisions, involving $OH(X^2\Pi)$,[2–18] $NO(X^2\Pi)$,[19–25] $NH(c^1\Pi)$,[26,27] $NH(A^3\Pi)$,[28] and $N_2(C^3\Pi_u)$.[29] In many of these studies, preferential production of one or the other Λ-doublet level has been interpreted by analysis of the evolution of the molecular orbitals of the precursor species which correlate with the unfilled π molecular orbital in the diatomic product.[3,4,7–13,15–18,20–22,27,28,30,31]

Crucial in this analysis is the correct identification of the electronic symmetry of the two Λ-doublet levels: In the high-J limit, for one level the wave function is symmetric with respect to reflection in the plane of rotation of the molecule, while in the other level the wave function is antisymmetric. There has been considerable disagreement concerning the electronic symmetry of Λ-doublet levels probed by the P, Q, or R branch lines of Σ–Π electronic transitions.[3,4,7,11,13,29,30,32–37] Additional confusion surrounded the possible reversal of the symmetry of Λ-doublet levels in molecules in $^2\Pi$ electronic states arising from a singly filled π orbital [e.g., $CH(X^2\Pi)$ or $NO(X^2\Pi)$] and those in molecules with a π^3 electron occupancy [e.g., $OH(X^2\Pi)$ or $CN(A^2\Pi)$].[4] The considerable controversy surrounding the source of OH interstellar maser emission is a striking illustration of the importance of a correct and absolute identification of the Λ doublet levels.[38]

In two recent articles, Alexander, Pouilly, and Dagdi-gian,[39,40] following earlier work by Green and Zare,[41] have presented a clear method for analyzing the reflection symmetry of the electronic wave function for molecules in Π electronic states. This analysis was carried out in detail for the case of $^1\Pi$, $^2\Pi$, and $^3\Pi$ electronic states. The measure of the reflection symmetry of the electron distribution was taken to be the expectation value of the operators $\sigma_v(xz)$ and $\sigma_v(yz)$ which represent reflection of the *spatial* coordinates of all the electrons in a plane containing the molecular axis, which we assume to define the molecule frame z axis. In those articles,[39,40] the third Euler angle γ specifying the orientation of the molecule with respect to the space-fixed coordinate system was set equal to 0, so that the plane of rotation coincides, in the high-J limit, with the xz and yz planes for $M = 0$ and $M = J$, respectively. Physically, the plane of rotation is perpendicular to **R**, the angular momentum of nuclear rotation; however, for large J, it will also be perpendicular to **N** and **J**. The reflection operator, as defined above, involves only the *spatial*, not the *spin*, coordinates of the electrons. This measure of the electronic reflection symmetry is particularly appropriate to interpretations of reactions and photodissociation processes in which arguments based on the evolution of the molecular orbitals of the precursor species are used to interpret the preferential production of a given Λ doublet.

Once the electronic symmetry of the electronic distribution has been properly identified, it is useful to develop an accepted and simple nomenclature which can then be used *without recourse to subtle analysis* by the community of scientists interested in the dynamics of diatomic and triatomic molecules. This is the goal of the present article. Several different notations have been presented in the past. In particular, the notation Π^+ and Π^- (or, equivalently, π^+ and π^- or Λ^+ and Λ^-) has been often used,[3,5,6(a),7,8,9(a),10–13,15,16,18–22,25,30,38,42] but the meaning of Π^+ and Π^- has varied. This particular notation has considerable appeal, but it is our belief that Π^+/Π^- is tainted by

past incorrect usage and should be abandoned to avoid further confusion. Moreover, notation similar to Π^+/Π^- is in wide use and denotes several different meanings, e.g., the sign of Λ in $\exp(-i\Lambda\varphi)$, the reflection symmetry with respect to an arbitrarily defined body-fixed plane containing the internuclear axis, or the specific linear combination of the $|n\Lambda S\Sigma>$ and $|n, -\Lambda S, -\Sigma>$ $\Lambda \neq 0$ electronic basis functions that can interact through the $B\,\mathbf{R}^2$ and spin–orbit operators with Σ^+ and Σ^- states.[43] There is precedent in the spectroscopic literature for such a change in notation, namely the replacement of the c/d notation by e/f to distinguish the rotation-independent parity of the Λ-doublet wave functions.[44]

The accepted spectroscopic e/f notation[44] refers only to the total parity, exclusive of rotation,[43] of the two Λ-doublet components. Furthermore, the e/f labels cannot be unambiguously correlated with the reflection symmetry of the electronic wave functions; for a $^2\Pi$ molecule, for example, the wave functions of the e Λ doublet are *symmetric* with respect to reflection for levels in the F_1 manifold but *antisymmetric* for levels in the F_2 manifold.[39] It is also important to adopt a notation which will apply equally to Π states arising from a π^1 or π^3 electronic configuration.

Finally, it will be desirable to have notation which can also be applied to molecules in states of higher electronic momentum, such as $\text{CH}(A\,^2\Delta)$,[45] $\text{NH}(a\,^1\Delta)$, or $\text{N}_2(W\,^3\Delta_u)$, or to the l doublet levels of a degenerate vibrational bending mode of a linear polyatomic molecule.[46,47] Preferential l-doublet populations have been seen experimentally,[48,49] and can be anticipated from theory,[50] in inelastic collisions involving HCN^{48} and CO_2.[49,50] Similar effects might be expected in, for example, photodissociation processes yielding CO_2 in the (01^10) vibrational manifold.[51]

In the next section we propose and justify a new notation for Λ-doublet levels, namely $\Pi(A')$ and $\Pi(A'')$ electronic states, $\Delta(A')$ and $\Delta(A'')$ for Δ states, etc. A brief conclusion follows.

II. A NEW NOTATION FOR Λ-DOUBLET LEVELS OF ROTATING MOLECULES IN $^{2S+1}\Lambda$ ELECTRONIC STATES

The measure of the symmetry of the electron distribution in a Π electronic state which we have proposed earlier[39,40] is the expectation value of the operators $\sigma_v(xz)$ and $\sigma_v(yz)$ which represent reflection of the molecule-fixed spatial coordinates of all the electrons in a plane containing the molecular axis, which we assume to define the molecule-frame z axis. The reflection operator involves only the spatial, not the spin, coordinates of the electrons. By this choice the same measure of electronic symmetry can be applied to wave functions in a Hund's case (a) limit,[1,52] where the spin is coupled to the molecule-frame z axis, and to wave functions in a case (b) limit,[1,52] where the spin is coupled to the space-frame Z axis.

The Hund's case (a) limit is valid for molecules in $^2\Pi$ and $^3\Pi$ states at low J, and for molecules in $^1\Pi$ states at all values of J. In this limit the electronic wave functions can be characterized by a well-defined plane of symmetry *only* for the $^1\Pi$ states and for the F_2 spin–orbit manifold of the $^3\Pi$

TABLE I. Symmetry with respect to reflection of the spatial coordinates of all the electrons, for molecules in Π electronic states—Hund's case (a) limit.

State	Spin–orbit manifold	e levels[a]	f levels[a]
$^1\Pi$		A'	A''
$^2\Pi$	F_1	N	N
	F_2	N	N
$^3\Pi$	F_1	N	N
	F_2	A''	A'
	F_3	N	N

[a] The states denoted by N are not eigenfunctions in the operator for reflection of the electronic spatial coordinates and thus cannot be characterized by a unique plane of symmetry.

state. The symmetries of the electronic wave functions in these states are given in Table I; here we designate *symmetric* with respect to reflection as A' and *antisymmetric*, as A''. In this table we have characterized the two Λ-doublet levels by the spectroscopic e/f label,[44] which is related to the total parity—that is, the symmetry with respect to inversion in the laboratory of all the coordinates.[52,53] In the case (a) limit, the electronic wave functions in both spin–orbit manifolds of the $^2\Pi$ state and the F_1 and F_3 manifolds of the $^3\Pi$ state cannot be characterized by a unique plane of symmetry for reflection of the spatial coordinates of the electrons; in other words the expectation value for the operator corresponding to reflection of the electronic spatial coordinates vanishes.

In all cases the symmetry characteristics are *independent* of the electron occupancy of the Π state in question, e.g., π, $\sigma\pi$, π^3, $\sigma\pi^3$, $\pi\delta$ and all three $^2\Pi$ state arising from $\pi^2\pi'$. To see this, consider a molecule in a $^2\Pi$ state, for example, with a nominal π configuration, e.g., NO, for which the dominant configuration is $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^2 1\pi^4 2\pi$. In a multireference description of this state, this configuration would mix with double excitations, such as $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 1\pi^4 2\pi^3$. The latter is a π^3 configuration. For these two configurations to mix, the reflection symmetry must obviously be the same and thus independent of electron occupancy.

At high J, a Hund's case (b) description is appropriate for molecules in $^2\Pi$ and $^3\Pi$ electronic states. In this limit the electronic wave function in *all* the spin–orbit manifolds of the $^2\Pi$ and $^3\Pi$ states can be characterized by a definite reflection symmetry. This is summarized in Table II. Note that the

TABLE II. Symmetry with respect to reflection of the spatial coordinates of all the electrons, for molecules in Π electronic states—high J limit.

State	Spin–orbit manifold	e levels	f levels
$^1\Pi$		A'	A''
$^2\Pi$	F_1	A'	A''
	F_2	A''	A'
$^3\Pi$	F_1	A''	A'
	F_2	A'	A''
	F_3	A''	A'

reflection symmetry of the wave functions in the F_2 manifold of the $^3\Pi$ state actually *reverses* from low J to high J.[40] Again, the symmetry characterization in Table II is *independent* of electron occupancy.

At intermediate values of J, the electronic wave functions for $S \neq 0$ Λ-doublet levels are, strictly speaking, not eigenfunctions of this reflection operator; in other words, the expectation value for the operator corresponding to reflection of the electronic spatial coordinates in the plane of rotation is nonzero but not equal to $+1$ or -1. The fractional A' or A'' character of a Λ-doublet level can be calculated by Eq. (25) of Ref. 39 for a $^2\Pi$ state and by Eq. (15) of Ref. 40 for a $^3\Pi$ state (setting $M = J$ in both cases). While this symmetry is not a rigorous quantum label, the Λ doublet levels can still be uniquely characterized by reference to their high-J limiting behavior.

Spectroscopic techniques—both resolved emission studies and laser fluorescence excitation of nonemitting products—have been widely used to determine populations in symmetric as compared to antisymmetric Λ-doublet levels. The most convenient electronic band system for obtaining the populations of individual Λ-doublet levels in a Π electronic state is a perpendicular ($\Delta\Lambda = \pm 1$) transition to a Σ electronic state. If electronically excited Π molecules are produced in the process under investigation, rotationally resolved emission to a Σ state can be employed to obtain the Λ-doublet populations. Alternatively, tunable laser fluorescence excitation to an excited Σ state can provide these populations for a nonemitting Π state. (In Π–Π and Δ–Π transitions each rotational "line" consists of a closely space pair of lines corresponding to transitions from both Λ-doublet levels.[1])

At moderate to high values of J, when $BJ > A$ so that the molecule in the Π state is near the case (b) limit, the strongest lines in a Π–Σ^+ or Π–Σ^- transition are those for which $\Delta J = \Delta N$.[1] These so-called main branch lines are labeled P_i, Q_i, and R_i, where $i = 1,2,...$. As has been discussed previously by Alexander, Dagdigian, and Pouilly,[39,40] *irrespective of the multiplicity of the Π state*, in the high-J limit, main-branch Q lines of a Π–Σ^+ transition probe levels which are antisymmetric with respect to reflection of the spatial coordinates in the plane of rotation while main-branch P and R lines probe levels which are symmetric. More generally, the Π–Σ^+ branches with ΔN even probe antisymmetric levels, while odd ΔN branches probe symmetric levels. This is *reversed* for a Π–Σ^- transition: Even ΔN branches probe *symmetric* levels, while odd ΔN branches probe levels which are *antisymmetric*.

Because of this simple connection for the Λ-doublet levels between spectroscopic branches and the reflection symmetry, which is the relevant quantity in any mechanistic interpretation of a reactive or photodissociative process, and because the reflection symmetry is independent of the electron occupancy of the Π state in question, we propose that this reflection symmetry be used to label the Λ-doublet levels, as follows[54]:

All series of levels in which the electronic wave function at high J is symmetric with respect to reflection of the spatial coordinates of the electrons in the plane of rotation (Table

II) will be designated $\Pi(A')$ levels for all values of J, and all those in which the electronic wave function is antisymmetric with respect to reflection (Table II) will be designated $\Pi(A'')$ levels.

If desired, $\Pi(A')$ and $\Pi(A'')$ may be written as $\Pi_{A'}$ and $\Pi_{A''}$. This is left as a matter of choice between author and typesetter. In this paper, we have chosen $\Pi(A')$ and $\Pi(A'')$.

This notation places emphasis on the fact that the effective point group of a rotating molecule is C_s, for which case A' and A'' are the appropriate labels for the irreducible representations. We note that this notation can be related to the total parity when expressed in terms of the case (b) rotational quantum number N[55]: $\Pi(A')$ levels have parity $(-1)^N$, while $\Pi(A'')$ levels have parity $(-1)^{N+1}$. This again emphasizes that the proposed notation is rigorous only when case (b) applies, i.e., when N is a good quantum number.

An alternative measure of the symmetry of the electron distribution which has been proposed[34] is the expectation value of the operator

$$\sum_i (\cos^2 \varphi_i - \sin^2 \varphi_i) , \tag{1}$$

where φ_i is the azimuthal angle of the ith electron with respect to the molecular axis and the sum extends over all the electrons. If the expectation value of this operator is positive, then electron density is preferentially in the xz plane; if negative, then preferentially in the yz plane. The disadvantage of this measure, as compared to the reflection symmetry, is that the expectation value $\sum_i (\cos^2 \varphi_i - \sin^2 \varphi_i)$ is dependent on the electron configuration of the Π state in question, whereas the reflection symmetry *is not*. This is illustrated clearly in Fig. 1, which illustrates both the reflection symmetry and
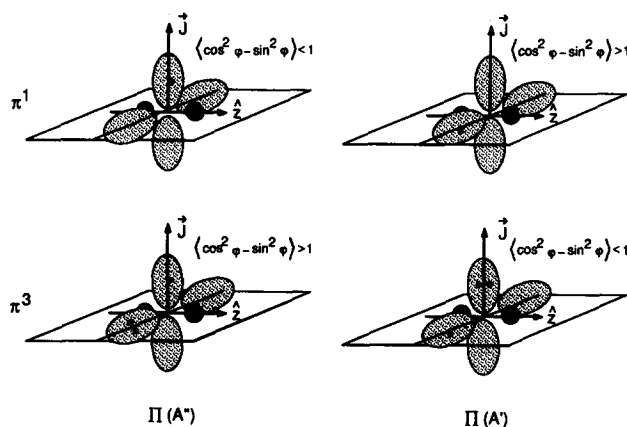

FIG. 1. Illustration of the electronic symmetry of the two Π Λ-doublet levels arising from a single π electron and three π electrons. In the high-J limit, the total angular momentum of the molecule J is perpendicular to the plane of rotation, which contains the molecular axis ($\hat{z}$). For $M \simeq J$ the plane of rotation coincides with the molecule-frame yz plane, while for $M \simeq 0$, with the molecule-frame xz plane. Also shown is the expectation value of $\sum_i (\cos^2 \varphi_i - \sin^2 \varphi_i)$, where φ_i is the azimuthal angle of the ith π electron around the z axis; here we assumed $M \simeq 0$, so that the x axis lies in the plane of rotation.

the expectation value of $\Sigma_i (\cos^2 \varphi_i - \sin^2 \varphi_i)$ for a hypothetical molecule with either a π^1 or π^3 electron occupancy.

Two alternative nomenclatures have been proposed recently.[9(b),17] Both of these notations, namely Π_B and $\Pi_B{}^9$ and $\pi(\|J)$ and $\pi(\perp J)$,[17] refer to the orientation of the unpaired $p\pi$ electron lobe with respect to the angular momentum vector **J**. In one set of levels [Π_B or $\pi(\|J)$] the $p\pi$ lobe is parallel to **J**, and hence perpendicular to the plane of rotation in the high J limit, while for the other [Π_∞ or $\pi(\perp J)$], the $p\pi$ lobe is the plane of rotation. We believe that the notation proposed here, $\Pi(A')$ and $\Pi(A'')$ is preferable for two reasons:

(1) The $\Pi(A')/\Pi(A'')$ notation has the advantage that it focuses upon the reflection symmetry of the Λ-doublet level, which is the property of greatest relevance for collision dynamics.

(2) This notation can also be generalized to Δ states by writing $\Delta(A')$ and $\Delta(A'')$ and to l-doublet levels of linear polyatomic molecules by writing $l(A')$ and $l(A'')$.

III. CONCLUSION

We have proposed a simple notation for Λ-doublet levels in linear molecules, namely the general label $\Lambda(A')$ and $\Lambda(A'')$, which becomes for Π states, $\Pi(A')$ and $\Pi(A'')$, etc. The A' levels are those for which the high-J limit the electronic wave functions are symmetric with respect to reflection of the spatial coordinates of the electrons in the plane of rotation of the molecule. For the A'' levels, on the other hand, the electronic wave functions are *antisymmetric* with respect to reflection in the plane of rotation. We emphasize that this notation is meant to supplement, and *not replace*, the accepted spectroscopic e/f labeling and the total parity quantum number. The $\Lambda(A')/\Lambda(A'')$ notation provides a simple, direct connection both with orbital correlation analyses of reaction and photodissociation mechanisms and with relative spectroscopic intensities used in probes of these processes. We believe that adoption of the present nomenclature will greatly help to eliminate future disagreement and confusion on the subject of the electronic symmetry of Λ-doublet levels.

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[54]In the F_2 manifold of a $^3\Pi$ state the expectation value of σ_v reverses in sign in going from the case (a) limit at low J to the case (b) limit at high J (Ref. 40). In this instance, in addition to using the $\Pi(A')/\Pi(A'')$ labeling, which is labeling by correlation with the high-J limit, it may be worthwhile to give the actual value of $\langle \sigma_v \rangle$, calculated as described in Ref. 40. A similar complication might arise for other states should non-Born–Oppenheimer perturbations (Ref. 43) lead to a significant contamination of the state in question with states of different Λ or different multiplicity.

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