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Clarification of the electronic asymmetry in Π-state Λ doublets with some implications for molecular collisions

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The asymmetry of the orbital part of the electronic wave functions and electronic charge distributions in $^1\Pi$, $^2\Pi$, and $^3\Pi$ Λ doublets is carefully examined, to clear up considerable past confusion on this subject. The results are: (1) For $^1\Pi$ and $^3\Pi_{\Omega=1}$ states the electronic wave function in the e Λ-doublet levels is symmetric with respect to reflection in the plane of rotation of the molecule and, in the f levels, antisymmetric. (2) For $^2\Pi$ and $^3\Pi_{0,2}$ states, in the Hund's case (a) limit the electronic distributions in both Λ-doublet levels are cylindrically symmetric. (3) As the case (b) limit is approached, the F_1 e and F_2 f wave functions of a $^2\Pi$ state acquire an increasing degree of symmetric character with respect to reflection in the plane of rotation, while the F_1 f and F_2 e levels acquire antisymmetric character. In a $^2\Sigma^+$–$^2\Pi$ radiative transition, the main branch P and R lines probe $^2\Pi$ levels which are symmetric with respect to reflection in the plane of rotation while the main branch Q lines probe levels which are antisymmetric. The reflection symmetry of Π-state electronic wave functions is shown to be independent of the number of π electrons, while the cylindrical asymmetry of the electronic charge distribution does depend on the electron occupancy. This formal analysis is used to draw implications for product Λ-doublet populations in photodissociation and reactive processes leading to Π-state molecules, and for collisions of Π-state molecules with surfaces.

I. INTRODUCTION

In diatomic molecules in electronic states of Π symmetry, 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] Three research groups have reported preferential population of the lower Λ doublets of the OH molecule$(X\,^2\Pi)$ in the H + NO$_2$→OH + NO reaction.[2–4] Specific Λ-doublet preferences were subsequently seen in a number of OH producing reactions,[5] in the scattering of NO$(X\,^2\Pi)$ from metal surfaces,[6] and in OH and NH$(c^1\Pi)$ formed in the photodissociation of H$_2$O,[7] HONO,[8] H$_2$O$_2$,[9,10] HNO$_3$,[10] and NH$_3$.[11] Nonstatistical population of Λ doublets has also been observed in rotational energy transfer in $^1\Pi$ excited states of the alkali dimers[12–15] and has been postulated as the source of OH and CH interstellar maser emission.[16–19] Also Λ-doublet effects have been seen in the Ar(^3P) + N$_2$O→Ar + N$_2(C\,^3\Pi_u)$ energy transfer process[20] and in the photofragmentation spectroscopy of CH$^+(A\,^1\Pi)$.[21]

In much of this previous work anomalous Λ-doublet populations have been interpreted[3,4,7,8–12,15–17,20] in terms of a difference in the π-electron wave function in the two Λ-doublet levels. In one level the wave function is symmetric with respect to reflection in the plane of rotation of the molecule; in the other level the wave function is antisymmetric. Unfortunately, there exists in the literature considerable disagreement between those authors[3,7,10,16,17,19–23] who associate the antisymmetric wave function with the Λ-doublet level which is connected by Q lines to a Σ^+ state and those authors[9,12,15,18] who associate this wave function with the level connected by P and R lines. Additionally, it has been

postulated[4] that the symmetry of the Λ-doublet wave functions is reversed in molecules with a π^3 electron occupancy such as OH$(X\,^2\Pi)$ as compared with molecules with a singly filled π orbital such as CH$(X\,^2\Pi)$ or NaK$(C\,^1\Pi)$. This has led to some controversy[3,4,7] concerning the interpretation of the preferential population of the lower OH Λ doublet observed in the H + NO$_2$ reaction. A particularly nice discussion of the properties of the OH Λ-doublet wave functions has been given recently by Andresen and co-workers.[7(b)]

In the present article we clarify the reflection symmetry and the asymmetry of the electron distributions in $^1\Pi$, $^2\Pi$, and $^3\Pi$ Λ doublets, discussed, respectively, in Secs. II, III, and IV. Obviously, the correct assignment of the Λ doublet is a necessary requirement in the development of accurate physical models for the interpretation of Λ-doublet effects in inelastic and reactive collisions. Section V presents some implications of the present analysis for the study of various kinetic processes. A brief conclusion follows.

II. $^1\Pi$ ELECTRONIC STATES

The molecular wave functions can be written as[19,23]

$$|JM\Lambda\ e/f\rangle = 2^{-1/2}[|JM\Lambda\rangle|\Lambda\rangle + \epsilon|JM,-\Lambda\rangle|-\Lambda\rangle],$$

$$(1)$$

where $\epsilon = \pm 1$; $|\Lambda\rangle$ designates the electronic wave function with projection $\Lambda = +1$ of the electronic angular momentum along the body-fixed z axis (taken to be the internuclear axis); and J is the total angular momentum with projection M along the space-fixed Z axis. We will use upper and lower case to designate, respectively, the space- and body-fixed axes. For simplicity the quantum number Λ will be sup-

pressed, except where explicitly needed. We will choose the symmetry of the electronic wave functions consistent with contemporary spectroscopic convention,[24] so that the symmetry index $\epsilon = +1$ corresponds to wave functions of total parity $(-1)^J$, denoted e levels,[25] and the index $\epsilon = -1$ corresponds to wave functions of total parity $(-1)^{J+1}$, denoted f levels.[25]

The molecular rotational wave functions in Eq. (1) are given by

$$|JM\Lambda\rangle = [(2J+1)/4\pi]^{1/2} D^{J*}_{M\Lambda}(\alpha\beta, \gamma = 0),\qquad(2)$$

where $D^J_{M\Lambda}$ is a rotation matrix element[26] and $(\alpha\beta\gamma)$ are the Euler angles which specify the orientation of the body frame with respect to the XYZ axes. We use active rotations as defined by Brink and Satchler.[24,26] In a diatomic molecule, the choice of the third Euler angle γ is arbitrary but must be made consistently for both the rotational and electronic parts of the wave function.[24,27] We have chosen $\gamma = 0$ here and have normalized accordingly, so that for $\beta = \pi/2$ the x axis lies along the negative Z axis.

A clear measure of the asymmetry of the electron distribution will be given by the expectation values of the operators $\sigma_v(xz)$ and $\sigma_v(yz)$ which represent reflection of the spatial coordinates of all the electrons. An expectation value of ± 1 would indicate that the electronic wave function is either symmetric or antisymmetric with respect to reflection; an expectation value of 0 would indicate that the e/f Λ doublets are not eigenfunctions of this reflection operator. These expectation values can be written

$$\langle\sigma_v(qp)\rangle_{JMe/f} = 1/2 \sum_{\Lambda,\Lambda'} (-1)^G \langle\Lambda'|\sigma_v(qp)|\Lambda\rangle S_{\Lambda'\Lambda}(J,M),$$
$$(3)$$

where $qp = xz$ or yz,

$$G = 1 \text{ for } \Lambda \neq \Lambda' \text{ in f symmetry}\qquad(4a)$$

and

$$G = 0 \text{ otherwise}.\qquad(4b)$$

Also, in Eq. (3) the function $S_{\Lambda'\Lambda}(J,M)$ is defined following the paper of Green and Zare[23] as

$$S_{\Lambda'\Lambda}(J,M) = [(2J+1)/4\pi] \int_0^{2\pi} d\alpha$$
$$\times \int_0^\pi \sin\beta \, d\beta \, D^J_{M\Lambda'}(\alpha\beta 0) D^{J*}_{M\Lambda}(\alpha\beta 0).\qquad(5)$$

It is easy to show that $S_{\Lambda'\Lambda}(J,M) = S_{\Lambda\Lambda'}(J,M)$.
We have[24,28,29]

$$\sigma_v(xz)|\Lambda\rangle = (-1)^\Lambda|-\Lambda\rangle\qquad(6)$$

and

$$\sigma_v(yz)|\Lambda\rangle = |-\Lambda\rangle.\qquad(7)$$

Thus, Eq. (3) yields

$$\langle\sigma_v(xz)\rangle_{JMe/f} = -\epsilon S_{1,-1}(J,M)\qquad(8)$$

and

$$\langle\sigma_v(yz)\rangle_{JMe/f} = \epsilon S_{1,-1}(J,M).\qquad(9)$$

As discussed by Green and Zare[23] for $J = M \gg 1$ the $\mathbf{J}$ vector lies along the Z axis and must also be perpendicular to the plane in which the molecule rotates. Because the Euler

angle γ has been taken to be zero, this implies that the yz plane coincides with the XY plane (the plane of rotation) in this large J limit. Furthermore,[23]

$$S_{1,-1}(J,J) = J/(J+1),\qquad(10)$$

which approaches unity as $J \to \infty$. Thus we see from Eq. (9) that in the $J = M \gg 1$ limit, where the yz plane is the plane of rotation, the e Λ-doublet level is symmetric with respect to reflection in this plane, while the f level is antisymmetric.

For $M = 0$ and J large, the $\mathbf{J}$ vector must lie along the y axis,[23] so that the xz plane is the plane of rotation. As shown by Green and Zare,[23]

$$S_{1,-1}(J,0) = -1,\qquad(11)$$

so that in this limit we see from Eq. (8) that the e Λ-doublet level is again symmetric with respect to the plane of rotation, while the f level is again antisymmetric.

As discussed by Gwinn et al.,[16] another measure of the asymmetry of the electron distributions is given by $\langle x^2 - y^2\rangle \sim \langle\cos^2\phi - \sin^2\phi\rangle$ where ϕ refers to the azimuthal orientation of the electrons in the body frame. As derived in Appendix A,

$$\langle\Lambda'|\cos^2\phi - \sin^2\phi|\Lambda\rangle = 1/2(-1)^{(n+1)/2}\delta_{\Lambda',\Lambda\pm2},$$
$$(12)$$

where n designates the number of unpaired π electrons $(n = 1,3)$. Following Eq. (3), we find

$$\langle\cos^2\phi - \sin^2\phi\rangle_{JMe/f} = 1/2(-1)^{(n+1)/2}\epsilon S_{1,-1}(J,M).\qquad(13)$$

With Eqs. (10) and (13) we see that in the $J = M \gg 1$ limit, where the yz plane is the plane of rotation, the electron distribution in the e Λ-doublet level is oriented preferentially in this plane in the case of a singly filled π orbital [as, e.g., $Li_2(B\,^1\Pi_g)$ or $NaK(C\,^1\Pi)$], but oriented preferentially perpendicular to this plane, and consequently along $\mathbf{J}$, in the case of a π^3 electron occupancy (EO) [as, e.g., $NH(c^1\Pi)$]. The situation is reversed for the f levels.

In the $J \gg 1$, $M = 0$ limit, where the xz plane is the plane of rotation, we see from Eq. (11) that the electron distribution in the e Λ-doublet level of a molecule with a π^1 EO is now oriented preferentially along the x axis *but still in the plane of rotation*, while for a π^3 EO the electron distribution is oriented preferentially along the y axis *but still perpendicular to the plane of rotation*. Again, the situation is reversed for the f levels.

The reader should note that the reflection symmetry of the electronic wave function is independent of the number of occupied π orbitals. However, the cylindrical asymmetry of the electronic distribution does depend on the electron occupancy.

For a π^1 EO our characterization of the electron distribution in the $^1\Pi$ Λ doublets agrees with that of many previous authors[11,19–22] but is reversed from that of Zare, McCaffery, and their co-workers.[12,15]

In their analysis of the a $^1\Pi$ molecule with a π^1 EO, Green and Zare[23] assigned the relative phases of the $+\Lambda$ and $-\Lambda$ wave functions oppositely from the now accepted convention,[24,28–30] which is based on the symmetry properties of the spherical harmonics,[26] so that the sign of the $\langle\Lambda'|\cos^2\phi - \sin^2\phi|\Lambda\rangle$ electronic matrix element would

be reversed from that given in Eq. (12). With this convention the symmetry index $\epsilon = +1$ in Eq. (1) would be associated with the f levels [parity $(-1)^{J+1}$] and $\epsilon = -1$ with the e levels [parity $(-1)^{J}$]. As demonstrated by Green and Zare,[23] within this phase convention the electronic distribution for the $\epsilon = +1$ levels would be oriented preferentially perpendicular to the plane of rotation; and for the $\epsilon = -1$ levels, in the plane of rotation. Thus the interpretation by Green and Zare[23] of the electronic asymmetry of Λ doublets in a $^1\Pi$ state with a π^1 EO is completely correct within the phase convention used by these authors.

III. $^2\Pi$ ELECTRONIC STATES

We shall describe a $^2\Pi$ electronic state first in a Hund's case (b) representation. The rotational wave functions are written as[31]

$$|JMN\Lambda e/f\rangle = \sum_{M_N M_S} (NM_N SM_S|JM)|NM_N\Lambda SM_S\,\eta\rangle ,$$

$$(14)$$

where $N = J - S$ and M_N and M_S are the projections of N and S along the space-fixed Z axis. Here $(\cdots|\cdots)$ is a Clebsch–Gordan coefficient[26] and

$$|MN_N\Lambda SM_S\eta\rangle = 2^{-1/2}[(2N+1)/4\pi]^{1/2}$$

$$\times\left[D^{N*}_{M_N\Lambda}|\Lambda SM_S\rangle + \eta D^{N*}_{M_N-\Lambda}|-\Lambda,SM_S\rangle\right] , \quad (15)$$

where $\eta = \pm 1$. Since $S = 1/2$, two J levels are associated with each value of N, with F_1 and F_2 labels[1] denoting the levels of lower and higher energy, respectively, for a given J. Each J level is further split into two Λ-doublet levels. The parity of the $|NM_N\Lambda SM_S\eta\rangle$ case (b) functions is $(-1)^N\eta$.[29] For a state of even multiplicity the e label is associated with levels of parity $+(-1)^{J-1/2}$ and the f label with levels of parity $-(-1)^{J-1/2}$.[25] Since $S = 1/2$ we have $J = N \pm 1/2$. It is easy to see that the e label corresponds to $\eta = +1$ in Eq. (15) for $J = N + 1/2$ and to $\eta = -1$ for $J = N - 1/2$, while the f label corresponds to $\eta = -1$ in Eq. (15) for $J = N + 1/2$ and to $\eta = +1$ for $J = N - 1/2$. The e/f, F_1/F_2, J, N assignments for a $^2\Pi$ state are clarified in Fig. 1, which displays several rotational levels of OH($X\,^2\Pi$).[32]

The development of Sec. II can be followed similarly to show that

$$\langle \sigma_v(xz)\rangle_{JMN\Lambda e/f}$$

$$= \sum_{M_N M_S} (NM_N SM_S|JM)^2[-\eta S_{1,-1}(N,M_N)] . \quad (16)$$

In deriving this equation we have used the fact that σ_v operates only on the spatial coordinates of the electrons and is independent of spin. From a comparison of Eqs. (6) and (7) we see that the expression for $\langle\sigma_v(yz)\rangle_{JMN\Lambda e/f}$ will be identical to Eq. (16) without the minus sign inside the brackets. For $S = 1/2$ the triangular relation in the Clebsch–Gordan coefficient limits N and M_N to the values $J \pm 1/2$ and $M \pm 1/2$, respectively. Since, in general,[23]

$$S_{1,-1}(N,M_N) = -1 + |M_N|(2N+1)/[N(N+1)] , $$

$$(17)$$

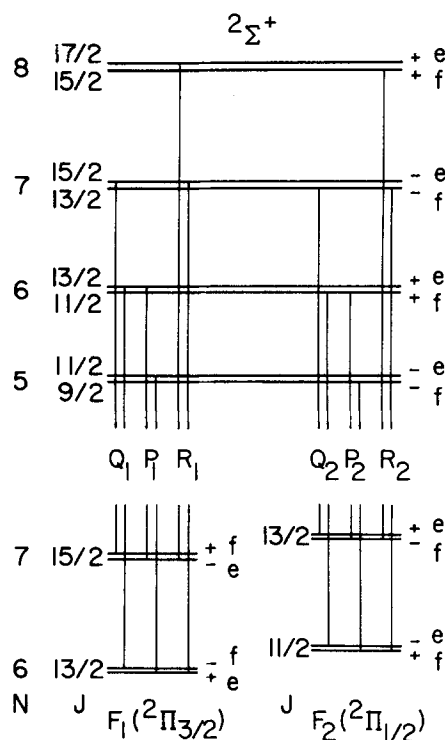it follows that for large J, $S_{1,-1}(N,M_N){\simeq}S_{1,-1}(J,M)$. We

FIG. 1. Allowed $^2\Sigma^+ - ^2\Pi$ [case (b)] radiative transitions. The ordering of the fine-structure levels and Λ doublets is appropriate for the OH molecule. The angular momenta J and N, as well as the overall parity and e/f labeling (Ref. 25), is indicated. Note that for OH the ordering of the Λ doublets reverses for $N\leqslant 4$ in the $F_2(^2\Pi_{1/2})$ manifold because of the approach to case (a) (Ref. 32).

can then use the orthogonality of the Clebsch–Gordan coefficients to obtain

$$\langle\sigma_v(xz)\rangle_{JMN\Lambda e/f}\simeq -\eta S_{1,-1}(J,M) \quad (18)$$

and

$$\langle\sigma_v(yz)\rangle_{JMN\Lambda e/f}\simeq\eta S_{1,-1}(J,M) , \quad (19)$$

which are equivalent to Eqs. (8) and (9). It is similarly possible to show, with the same reasoning, that

$$\langle\cos^2\phi - \sin^2\phi\rangle_{JMN\Lambda e/f} = 1/2(-1)^{(n+1/2)}\eta S_{1,-1}(J,M) , $$

$$(20)$$

where n again indicates the number of electrons in unfilled π orbitals.

Thus we can apply the same argument as in Sec. II to demonstrate that in case (b) at high J the $^2\Pi$ Λ-doublet level with $\eta = +1$ for a given JN is symmetric with respect to reflection in the plane of rotation, while the level with $\eta = -1$ is antisymmetric. Similarly for the $\eta = +1$ levels the electronic distribution is preferentially oriented in the plane of rotation for a π^1 electron occupancy and perpendicular to the plane of rotation for a π^3 EO, and vice versa for the $\eta = -1$ levels.

However, the e/f labels are associated with the $\eta = \pm 1$ levels differently depending on the value of N. Thus, for the Λ doublet corresponding to $J = N + 1/2$ the characterization of the electronic charge distribution is similar to that for a $^1\Pi$ state, namely the e Λ-doublet level is symmetric with respect to reflection in the plane of rotation.

By contrast, for the Λ doublet corresponding to $J = N - 1/2$ *the situation is reversed*; the e level is *antisymmetric* with respect to reflection in the plane of rotation.

At lower J it is more appropriate to use a case (a) basis. The wave functions are written as[33]

$$|JMF_1e/f\rangle = \cos\theta_J|JM,\Omega = 1/2,e/f\rangle$$
$$+ \sin\theta_J|JM,\Omega = 3/2,e/f\rangle \qquad (21)$$

and

$$|JMF_2e/f\rangle = -\sin\theta_J|JM,\Omega = 1/2,e/f\rangle$$
$$+ \cos\theta_J|JM,\Omega = 3/2,e/f\rangle , \qquad (22)$$

where θ_J ranges from 0 to $\pi/2$, with a value depending on the magnitudes of J, the rotational constant B, and the spin-orbit constant A.[34] In the case (a) limit $\theta_J \to 0$ for a regular[1] $^2\Pi$ state $(A > 0)$ and $\theta_J \to \pi/2$ for an inverted[1] $^2\Pi$ state $(A < 0)$. The $|JM\Lambda e/f\rangle$ functions are defined similarly to Eq. (1), namely,

$$|JM\Omega e/f\rangle = 2^{-1/2}[|JM\Omega\rangle|\Lambda = 1,\Sigma = \pm 1/2\rangle$$
$$+ \epsilon|JM - \Omega\rangle|\Lambda = -1,\Sigma = \mp 1/2\rangle] , \quad (23)$$

where the upper signs refer to the $\Omega = 3/2$ spin-orbit rotational levels and the lower signs, to the $\Omega = 1/2$ levels. In contrast to the case (b) wave functions [Eq. (15)], in Eq. (23) the e label corresponds to the positive combination $(\epsilon = +1)$ of the $|\Lambda\rangle$ and $|-\Lambda\rangle$ functions for both the F_1 and F_2 Λ doublets. At high J, when $BJ \gg A$, the angle θ_J approaches $\pi/4$ and, as will be demonstrated in Appendix B, the F_1 and F_2 wave functions expressed in the case (a) basis [Eqs. (21) and (22)] become identical to the $|JMN\rangle$ case (b) wave functions [Eqs. (14) and (15)].

It is possible to determine matrix elements of the reflection operators $\sigma_v(xz)$ and $\sigma_v(yz)$ in the case (a) basis, exactly as in Sec. II. We find

$$\langle JM\Omega'e/f|\sigma_v(pq)|JM\Omega e/f\rangle$$
$$= \mp \epsilon(1 - \delta_{\Omega',\Omega})S_{\Omega',\Omega}(J,M) , \qquad (24)$$

where the $+$ sign refers to reflection in the yz plane and the $-$ sign, to reflection in the xz plane. In deriving this equation we have used the fact that $S_{\Omega,\Omega'}(J,M) = S_{\Omega',\Omega}(J,M)$ for $\Omega = 1/2, \Omega' = 3/2$. The $(1 - \delta_{\Omega',\Omega})$ factor arises because of the implied integration over the electronic spin which causes the electronic matrix elements to vanish unless $\Sigma' = \Sigma$. Taking into account Eqs. (21) and (22), we find

$$\langle\sigma_v(xz)\rangle_{JMF_1e/f} = \mp 2\epsilon \sin\theta_J \cos\theta_J S_{1/2,-3/2}(J,M) \qquad (25)$$

and

$$\langle\sigma_v(yz)\rangle_{JMF_1e/f} = \pm 2\epsilon \sin\theta_J \cos\theta_J S_{1/2,-3/2}(J,M) , \qquad (26)$$

where the upper sign refers to the $F_1 \Lambda$ doublet and the lower sign to the $F_2 \Lambda$ doublet.

In analyzing Eqs. (25) and (26) we observe first that in the pure case (a) limit $(\theta_J = 0$ or $\pi/2)$ the expectation values of both reflection operators are zero, indicating that the Λ-doublet wave functions are not eigenfunctions of these two operators. As one moves from the case (a) to the case (b) limit, the expectation values approach unity in magnitude. Since one can show, for example, that $S_{1/2,-3/2}(J,J) = [(J - 1/2)/(J + 3/2)]^{1/2}$. The analysis of Sec. II can then

be followed to demonstrate that the wave function for the F_1 e Λ doublet level increasingly acquires a symmetric character with respect to reflection in the plane of rotation, while the F_1 f level increasingly acquires an antisymmetric character with respect to reflection in this plane. The situation is reversed for the $F_2 \Lambda$ doublets; the e levels increasingly acquire antisymmetric character and the f levels acquire symmetric character. Since, as will be demonstrated in Appendix B, in the case (b) limit the F_1 and F_2 levels correspond to $N = J \mp 1/2$, respectively, the analysis presented in this paragraph is entirely consistent with the analysis presented earlier in this section which was based on case (b) wave functions. Andresen and co-workers[7(b)] have similarly demonstrated how the reflection symmetry with respect to the plane of rotation becomes increasingly apparent as the case (b) limit is approached.

In the specific case of OH(X $^2\Pi$), the F_1 e levels lie below the F_1 f levels (Fig. 1), so that in the lowest state $[J = 3/2, F_1e]$ the elecronic wave function is symmetric with respect to reflection in the plane of rotation, to the extent that the $J = 3/2$ levels are not pure case (a). This is opposite to the prediction of Shapiro and Kaplan.[18]

It is also possible, as before, to look at matrix elements of the electronic operator $\langle\cos^2\phi - \sin^2\phi\rangle$. With Eqs. (12) and (23), and following Eq. (24), we find

$$\langle\cos^2\phi - \sin^2\phi\rangle_{JMF_1e/f}$$
$$= \pm(-1)^{(n+1)/2}\epsilon \sin\theta_J \cos\theta_J S_{1/2,-3/2}(J,M) , \quad (27)$$

where the $+$ sign refers to the $F_1 \Lambda$ doublet and the $-$ sign to the $F_2 \Lambda$ doublet. For the particular choice of $M = J$ and $n = 1$, Eq. (27) has been given already by Gwinn, Townes, and co-workers.[16,17]

We see that in the case (a) limit $(\theta_J = 0$ or $\pi/2)$ the electronic distribution will be cylindrically symmetric in all Λ-doublet levels, a conclusion also stated by Dixon and Field,[19] but without proof. As the mixing between the $\Omega = 1/2$ and $\Omega = 3/2$ spin-orbit manifolds increases, and θ_J begins to differ from the pure case (a) value, cylindrical asymmetry will appear. For a π^1 EO [as, e.g., in CH(X $^2\Pi$)] in the F_1 e Λ-doublet level the electronic distribution becomes oriented preferentially *in the plane of rotation* and in the F_1 f level, oriented preferentially *perpendicular* to the plane of rotation. The opposite applies to the $F_2 \Lambda$ doublets. For a π^3 EO [as, e.g., in OH(X $^2\Pi$)] the analysis is reversed; in particular, in the F_1 e level the electronic distribution becomes oriented preferentially *perpendicular* to the plane of rotation. As in our analysis of the reflection symmetry, the conclusions of this paragraph agree perfectly with those derived from the analysis of the case (b) wave functions.

The reader should observe that, equivalently to the case of $^1\Pi$ molecules, the reflection symmetry of the Λ-doublet levels is *independent* of the electron occupancy. However, the asymmetry of the electronic distribution in the Λ-doublet levels does depend on the electron occupancy, as discussed originally by Gwinn et al.,[16] but not recognized by Luntz, Andresen, and co-workers.[3,7]

In the past, various authors[11(b),17] have assigned the charge asymmetry in Π state Λ doublets based on reasoning by analogy with the case of an asymmetric top: Namely, the

upper Λ-doublet level was associated with the lower moment of inertia. This level has been assumed to correspond to the π electron lying perpendicular to the plane of rotation. The fallacy of this argument is demonstrated by the fact that the Λ-doubling parameter q, which determines the energy splitting between the e and f levels in the high J limit,[1,27,35] can be both positive or negative for $^2\Pi$ molecules with the same electron occupancy. An example would be CH($X\,^2\Pi$) with $q = 3.6 \times 10^{-5}$ cm^{-1} and CaH($A\,^2\Pi$) with $q = -6.4 \times 10^{-5}$ cm^{-1}.[35] In reality, the Λ-doublet splitting arises from spin-rotation and orbit-rotation coupling between the Π state in question and other Σ^+ and Σ^- states.[27] The moment of inertia should be calculated from the perturbed wave function, which depends on the admixture of Σ states with appropriate phases.

It will be relevant to the discussion in Sec. V to point out that for $^2\Sigma^+ - ^2\Pi$ spectroscopic transitions at moderate to high J, when the $^2\Pi$ molecule is no longer in a pure case (a) limit, the $F_1(N = J - 1/2)\,^2\Pi$ levels of e parity are probed by P_1- and R_1-branch lines and the levels of f parity by Q_1-branch lines.[1,28,32] The situation is reversed for transitions involving the $F_2\,(N = J + 1/2)\,^2\Pi$ levels. (The main branch[1] lines are now labeled P_2, R_2, and Q_2.) This is illustrated for the OH($X\,^2\Pi$) molecule in Fig. 1. From the discussion earlier in this section, we then conclude that in the case (b) limit, for transitions from both F_1 and F_2 levels the main branch P and $R\ ^2\Sigma^+ - ^2\Pi$ lines probe the $^2\Pi\ \Lambda$-doublet levels which are symmetric with respect to reflection in the plane of rotation, while the main branch Q lines probe levels which are antisymmetric with respect to this reflection. This is consistent with the classical limit argument presented by Sinha, Caldwell, and Zare,[36] whereby for $^2\Sigma^+ - ^2\Pi$ Q-branch transitions at large J the dipole oscillator lies along $\mathbf{J}$ and perpendicular to the plane of rotation and for P- and R-branch transitions the dipole oscillator lies in the plane of rotation and perpendicular to $\mathbf{J}$. Our association of the Λ-doublet levels with particular rotational branches agrees with the previous analysis of Luntz, Andresen, Wolfrum, and co-workers[3,7,10] but disagrees with that of Kinsey, Bersohn, and co-workers.[4,9]

IV. $^3\Pi$ ELECTRONIC STATES

We will not examine the case of $^3\Pi$ states in as much detail as was done for the $^1\Pi$ and $^2\Pi$ states. Nevertheless, some important general conclusions can be made, based on the results of Secs. II and III. In a case (a) basis the rotational wave functions for a $^3\Pi$ molecule are written

$$|JM\Omega = 2, e/f\rangle = 2^{-1/2}[\,|JM\,2\rangle\,|\Lambda = 1, \Sigma = 1\rangle$$
$$+ \epsilon|JM - 2\rangle\,|\Lambda = -1, \Sigma = -1\rangle\,]\,,$$
$$(28)$$

$$|JM, \Omega = 1, e/f\rangle = 2^{-1/2}[\,|JM\,1\rangle\,|\Lambda = 1, \Sigma = 0\rangle$$
$$+ \epsilon|JM - 1\rangle\,|\Lambda = -1, \Sigma = 0\rangle\,]\,, \quad (29)$$

and

$$|JM, \Omega = 0, e/f\rangle = 2^{-1/2}[\,|JM\,0\rangle\,|\Lambda = 1, \Sigma = -1\rangle$$
$$+ \epsilon|JM\,0\rangle\,|\Lambda = -1, \Sigma = 1\rangle\,]\,. \quad (30)$$

Similarly to Sec. II, since matrix elements of $\cos^2\phi - \sin^2\phi$,

$\sigma_v(xz)$, and $\sigma_v(yz)$ vanish unless the spin projection Σ is conserved, it follows that in the case (a) limit only the $\Omega = 1\ \Lambda$ doublets can be characterized by an electronic asymmetry. They behave like the Λ doublets of a $^1\Pi$ state, not only in this respect, but also, as is well known,[1,35] in the variation with J of the Λ-doublet splitting.

Electronic asymmetry in the $\Omega = 0$ and $\Omega = 2$ manifolds will arise, analogously to the $^2\Pi$ case, only by mixing of these two manifolds, which will take place with increasing J, as the orbit-rotation coupling increases. However, since this $\mathbf{J \cdot L}$ term in the rotational Hamiltonian will only couple case (a) states with $\Omega' = \Omega \pm 1$,[27,29,34,37] any mixing of the $\Omega = 0$ and $\Omega = 2$ manifolds will occur only as a second-order process. Thus, we might expect the electronic asymmetry in the $\Omega = 0$ and $\Omega = 2\ \Lambda$ doublets to become apparent at considerably higher values of J than for a comparable $^2\Pi$ state.

V. IMPLICATIONS FOR KINETIC PROCESSES
A. Photodissociation

In recent experiments nonstatistical Λ-doublet populations have been seen in the OH($X\,^2\Pi$) molecule produced in the photodissociation of H_2O,[7] HONO,[8] H_2O_2,[9,10] and HNO_3,[10] and in NH($c\,^1\Pi$) produced in the photodissociation of NH_3.[11] In each case the observations have been interpreted in terms of the rapid dissociation of a planar repulsive excited state, with the rotational motion of the nascent OH or NH molecules confined initially to this plane. Consideration of the orbital rearrangement which accompanies the photofragmentation, for example in NH_3, suggests that the electronic wave function of the NH fragment will be symmetric with respect to this plane. This would imply that the e Λ-doublet level will be preferentially formed, consistent with the experimental results.

Obviously, in the case of a $^2\Pi$ photofragment a prediction of nonstatistical Λ-doublet populations will be valid only at values of J for which there is substantial mixing of the $\Omega = 1/2$ and $\Omega = 3/2$ wave functions, since, as we have seen, in the pure case (a) limit neither Λ-doublet level can be characterized by its reflection symmetry. In this regard, Andresen and co-workers[7] have shown that the OH Λ-doublet population ratios as a function of N observed in the photodissociation of H_2O can be predicted from the mixing coefficients of the intermediate Hund's case rotational wave functions [Eqs. (21) and (22)].

Because the ratio of A to B is much larger in NO as compared to OH, one would expect to see nonstatistical Λ-doublet populations only at much higher J in the case of a NO($X\,^2\Pi$) photofragment. A possible test of this prediction would involve the study of the

$$\text{NCNO}^* \rightarrow \text{CN}(X\,^2\Sigma^+) + \text{NO}(X\,^2\Pi) \qquad (31)$$

process, already initiated by several groups.[38,39] If the excited NCNO* state is planar and of A'' symmetry, as suspected, then, because a $^2\Sigma^+$ wave function is of A' symmetry, the NO electronic wave function would have to be of A'' symmetry with respect to the four-atom plane. If, further, the release of the NO fragment were confined to this plane, then we would predict preferential population of the f Λ-doublet level in the $F_1(\Omega = 1/2)$ manifold and the e level in the $F_2(\Omega = 3/2)$

manifold), but only at high J where significant mixing of the case (a) wave functions begins to occur. The rotational distribution of the NO fragment has been studied,[38] although the individual Λ-doublet populations have not been extracted. A similar symmetry argument has been applied to H_2O photofragmentation dynamics by Andresen and co-workers.[7]

B. Reactive collisions

As discussed in the Introduction, the first evidence of nonstatistical Λ-doublet populations was seen in the reaction[2–4]

$$H + NO_2 \rightarrow NO(X\,^2\Pi) + OH(X\,^2\Pi). \tag{32}$$
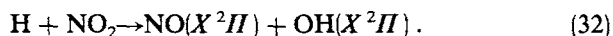
The original interpretation of this observation by Mariella and Luntz[3] was based on symmetry arguments. Our analysis (see Sec. III) demonstrates that this interpretation is indeed correct and is *independent* of the π electron occupancy of OH, contrary to the discussion of Kinsey and co-workers.[4]

It is interesting to compare reaction (32), which is assumed[3] to pass through a planar intermediate of A' symmetry, with the photodissociation of HONO, where the fragmentation has been postulated to involve a planar intermediate of A'' symmetry.[8] In both cases the OH fragment is found experimentally to be preferentially populated in the Λ-doublet levels which correspond in the high J, case (b) limit to an electronic wave function symmetric (A') with respect to reflection in the plane of rotation. Since the overall symmetry of the electronic wave functions of both products will conserve the symmetry of the wave function of the (assumed) planar HONO transition state, it follows that for reaction (32) the wave function of the NO product will be of A' symmetry with respect to the plane of rotation, while for the photodissociation process the NO wave function will be of A'' symmetry. This implies that any high J levels of NO which are present should display nonstatistical Λ doublet populations which reverse on going from the ground state reaction to the photodissociation reaction. The rotational distribution of the NO products in reaction (32) has not yet been explored experimentally, and unfortunately may not be possible for the photodissociation reaction, due to contamination with NO produced from the photodissociation of the NO_2 precursor.[40]

There has been considerable interest in reactions of Mg atoms with N_2O[41–44]:

$$Mg(^1S, ^3P) + N_2O \rightarrow MgO + N_2. \tag{33}$$
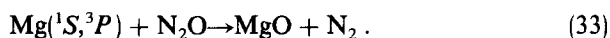
The MgO product can be formed in the ground $(X\,^1\Sigma^+)$ or low-lying $a\,^3\Pi$ and $A\,^1\Pi$ states. Recently, in flame experiments Ip, Field, and Cross[44] found that the populations in the $a\,^3\Pi, \Omega = 0$,e rotational levels were considerably enhanced relative to the populations in the $\Omega = 0$,f and $\Omega = 1,2$ e/f levels. These anomalous Λ-doublet populations could result either from collisional effects[45,46] subsequent to reaction (33) or as a direct consequence of dynamical constraints during this reaction itself.

The latter interpretation can be eliminated by means of the analysis developed in the present paper. MgO in the $a\,^3\Pi$ state is strongly case (a) with $B/A = 0.008$.[44,47] Thus, consistent with the discussion in Sec. IV, even if reaction (33) were to proceed over a planar surface and even if the rotation of

the nascent MgO product were constrained to this plane, we would predict nonstatistical Λ-doublet populations in the $\Omega = 0$ and $\Omega = 2$ rotational manifolds only at very high values of J where the deviation from case (a) becomes significant. Also, since the $\Omega = 1$ manifold behaves like a $^1\Pi$ state, with a clear electronic asymmetry even at low J, we would expect to see the largest Λ-doublet population anomalies in the $\Omega = 1$ products, if indeed these anomalies occurred as a result of the formation reaction (33).

C. Molecule–surface collisions

Luntz, Kleyn, and Auerbach[6] have studied collisions of a rotationally cold beam of NO molecules with a Ag(111) surface and observed extremely high rotational excitation in the scattered molecules. For final rotational quantum numbers $J' > 30.5$, the relative Λ-doublet populations indicate an increasing propensity to scatter molecules into the F_1 e and F_2 f levels. As discussed in Sec. III, these correspond to a partial symmetry of the π-electron density with respect to reflection in the plane of rotation of the molecule, perpendicular to J. As in the case of collisions of a $^2\Pi$ molecule with an atom,[18,19,48] a complete description of the dynamics will involve two electrostatic potentials, which correspond to the two possible symmetries of the electronic wave function of the impinging molecule with respect to reflection in the xz plane.[49] It may well be that the results of the experiments of Luntz et al.[6] contain useful information about the relative efficiency of inelastic scattering on these two potential surfaces. The details of the collision of a $^2\Pi$ molecule with an uncorrugated surface have been analyzed in another publication.[49]

VI. CONCLUSION

We have presented a careful review and analysis of the asymmetry of the orbital part of the electronic wave functions of Λ-doublets in states of Π symmetry. Our major conclusions are as follows:

(1) For rotational levels of $^1\Pi$ states, and $^3\Pi_{\Omega=1}$ states in the case (a) limit ($BJ \ll A$), the electronic wave function in the e Λ-doublet levels is symmetric with respect to reflection in the plane of rotation of the molecule and, in the f levels, antisymmetric with respect to reflection in this plane.

(2) For $^2\Pi$ and $^3\Pi_{\Omega=0,2}$ rotational levels in the case (a) limit the electronic distributions in both Λ-doublet levels are cylindrically symmetric.

(3) As J increases, the F_1 e and F_2 f levels of a $^2\Pi$ state acquire an increasing degree of symmetric character with respect to reflection in the plane of rotation, while the F_1 f and F_2 e levels acquire an increasing degree of antisymmetric character. In the case (b) limit ($BJ \gg A$) the electronic asymmetry in the F_1 manifold ($J = N + 1/2$) is equivalent to that of a $^1\Pi$ state, namely the e Λ-doublet levels are symmetric with respect to reflection in the plane of rotation. For the F_2 manifold ($J = N - 1/2$) the situation is reversed: The f levels are symmetric with respect to reflection in this plane. In either case, in a $^2\Sigma^+$–$^2\Pi$ radiative transition, the main branch P and R lines probe $^2\Pi$ levels which are symmetric with respect to reflection in the plane of rotation, while the

main branch Q lines probe levels which are antisymmetric.

(4) The cylindrical asymmetry of the electronic charge distribution in Π electronic states depends on the number of electrons in unfilled π orbitals. For an electron occupancy of π^1, the charge distribution is preferentially oriented in the plane of rotation for the Λ-doublet levels for which the wave function is symmetric with respect to reflection in this plane and preferentially oriented perpendicular to the plane of rotation for the levels for which the wave function is antisymmetric. This correlation is reversed for states arising from a π^3 electron occupancy.

This general analysis was used to draw some implications for various molecular processes, especially for those which proceed through a planar intermediate described by a wave function of unique C_s symmetry. In this case nonstatistical Λ-doublet populations should be seen, especially for products in $^1\Pi$ and $^3\Pi_1$ electronic states. For products in $^2\Pi$ or $^3\Pi_{0,2}$ electronic states, nonstatistical Λ-doublet populations will be seen only for J values large enough that a significant breakdown in the case (a) description of the wave function occurs.

Note added in proof: K. Kleinermanns and J. Wolfrum [J. Chem. Phys. **80**, 1446 (1984)] have recently reported preferential Λ-doublet populations in OH product from the hyperthermal $H + O_2$ reaction. Their interpretation is consistent with the analysis given here.

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APPENDIX A: CYLINDRICAL SYMMETRY OF Π WAVE FUNCTIONS

It is sufficient to consider only those electrons in the unfilled π orbitals. These orbitals will be expanded as LCAO's, namely (in Røeggen's notation[30])

$$|\pi_\lambda\rangle = \sum_{jkl} |jkl\lambda\rangle\langle jkl\lambda |\pi_\lambda\rangle , \tag{A1}$$

where j denotes the atomic center, and k and l index the atomic orbitals of azimuthal symmetry $\lambda = \pm 1$. We also have[30] $\langle jkl - \lambda |\pi_{-\lambda}\rangle = \langle jkl\lambda |\pi_\lambda\rangle$. For a singly occupied π orbital, the expectation value of the one-electron operator $\cos^2\phi - \sin^2\phi$ is just

$$\langle \pi_\lambda, |\cos^2\phi - \sin^2\phi |\pi_\lambda\rangle$$
$$= \langle \pi_\lambda, |1/2(e^{2i\phi} + e^{-2i\phi})|\pi_\lambda\rangle$$
$$= -1/2\delta_{\lambda',\lambda \pm 2} . \tag{A2}$$

This follows from the fact that the angular dependence of the atomic orbitals in Eq. (A1) is governed by the spherical harmonics $Y_{l\lambda}$.

For a π^3 electron occupancy the wave function can be described by Slater determinants, namely

$$|\Lambda = 1\rangle = |\pi_1\bar{\pi}_1\pi_{-1}| \tag{A3}$$

and

$$|\Lambda = -1\rangle = |\pi_{-1}\bar{\pi}_{-1}\pi_1| . \tag{A4}$$

It follows[50] that

$$\langle \Lambda' = \mp 1| \sum_{i=1}^{3}(\cos^2\phi_i - \sin^2\phi_i)|\Lambda = \pm 1\rangle$$
$$= -\langle \pi_{\lambda'= \mp 1}|\cos^2\phi - \sin^2\phi |\pi_{\lambda = \pm 1}\rangle . \tag{A5}$$

Furthermore, because of the Kronecker delta in Eq. (A2) we have

$$\langle \Lambda | \sum_i (\cos^2\phi_i - \sin^2\phi_i)|\Lambda \rangle = 0 . \tag{A6}$$

Equations (A2) and (A6) can be combined to give Eq. (13). This should be compared with a similar expression given by Brown *et al.*,[28] which we now see to be correct only for a π^1 electron occupancy.

The above argument applies to $^2\Pi$ states but could easily be extended to $^1\Pi$ or $^3\Pi$ states with a $\pi^3\sigma$ electron occupancy in which case the relevant Slater determinants would be written:

$$|\Lambda = 1,^3\Pi \rangle = |\pi_1\bar{\pi}_1\pi_{-1}\sigma| \tag{A7}$$

and

$$|\Lambda = 1,^1\Pi \rangle = 2^{-1/2}[|\pi_1\bar{\pi}_1\pi_{-1}\bar{\sigma}| + |\pi_1\bar{\pi}_1\bar{\pi}_{-1}\sigma|] ,\tag{A8}$$

and similarly for $\Lambda = -1$. In both cases Eq. (A5) is recovered.

APPENDIX B: CORRESPONDENCE BETWEEN HUND'S CASE (a) AND (b) WAVE FUNCTIONS FOR A $^2\Pi$ STATE

The transformation from the case (b) rotational wave functions [Eqs. (14) and (15)] to the case (a) functions [Eqs. (21)–(23)] depends on two key relations: First, the relation between the space-frame and body-frame spin functions, namely,[27]

$$|SM_S\rangle = \sum_{\Sigma} D_{M_S\Sigma}^{S*}(\alpha\beta 0)|S\Sigma \rangle ; \tag{B1}$$

and second, the relation for the product of two rotation matrix elements, namely,[26]

$$D_{M_N\Lambda}^{N*} D_{M_S\Sigma}^{S*} = (-1)^{M-\Lambda-\Sigma}\sum_J (2J+1)$$
$$\times\begin{pmatrix} N & S & J \\ M_N & M_S & -M \end{pmatrix}$$
$$\times\begin{pmatrix} N & S & J \\ \Lambda & \Sigma & -\Omega \end{pmatrix} D_{M\Omega}^{J*} . \tag{B2}$$

With these two relations it is possible to show that

$$[(2N+1)/4\pi]^{1/2} D_{M_N\Lambda}^{N*} |\Lambda SM_S\rangle$$
$$= \sum_{J\Sigma}(-1)^{N+2M-S-\Lambda-\Sigma}(2N+1)^{1/2} \tag{B3}$$
$$\times\langle NM_N SM_S|JM\rangle \begin{pmatrix} N & S & J \\ \Lambda & \Sigma & -\Omega \end{pmatrix} |JM\Omega\rangle|\Lambda\Sigma\rangle .$$

From this, with a little angular momentum algebra, one can

derive the following expression for the case (b) wave functions [Eq. (14)]:

$$|JM\Lambda e/f\rangle = (-1)^{N+2M-1}(2N+1)^{1/2}$$

$$\times\left[\begin{pmatrix} N & 1/2 & J \\ 1 & -1/2 & -1/2 \end{pmatrix}|JM,\Omega = 1/2\ \epsilon\rangle\right.$$

$$\left. - \begin{pmatrix} N & 1/2 & J \\ 1 & 1/2 & -3/2 \end{pmatrix}|JM,\Omega = 3/2,\epsilon\rangle\right],$$
(B4)

where the Hund's case (a) functions $|JM\Omega\epsilon\rangle$ are defined by Eq. (23) and where the relation between the case (a) symmetry index ϵ in Eq. (B4) and the case (b) symmetry index η in Eq. (15) is given by

$$\epsilon = \eta(-1)^{N+J-1/2}.$$
(B5)

By explicitly evaluating the $3j$ symbols we can simplify Eq. (B4) to obtain, for $N = J - 1/2$, Eq. (21) with $\epsilon = \eta$ and with

$$\sin\theta_J = [(J+3/2)/(2J+1)]^{1/2}$$
(B6)

and

$$\cos\theta_J = [(J-1/2)/(2J+1)]^{1/2}.$$
(B7)

These expressions for $\sin\theta_J$ and $\cos\theta_J$ have been derived previously by Hougen.[34] Similarly for $N = J + 1/2$ we obtain Eq. (22) with $\epsilon = -\eta$ and with $\sin\theta_J$ and $\cos\theta_J$ again given by Eqs. (B6) and (B7). We see that at high J, $\theta_J \simeq \pi/4$ as stated in Sec. III.

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