Analysis of chemical dynamics via Λ doubling: Directed lobes in product molecules and transition states

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Many molecular processes, such as chemical reactions, inelastic collisions, photodissociation, and surface scattering, yield selective populations of Λ-doublet states. The interpretation of such experiments has been difficult, so that little quantitative information could be extracted. Based on the results of our experiment on the photodissociation of H_2O, and upon calculations presented here, this situation becomes much better. We discuss processes which yield product $^2\Pi$ diatomics XY in which the Λ doublets are a manifestation of two different orientations of an unpaired $p\pi$ electron orbital. Chemical dynamics which produce such selective populations indicate a stereochemical effect: for example, the unpaired $p\pi$ orbital in the XY may point in the direction of the previous bond between XY and the transition complex, and, in an energetic breakup, would have a spatial relationship to J, the total angular momentum of XY. We describe here: (a) the directions of the orbitals at high J, (b) the effect of J, and of the particular XY studied, upon the analysis, so that J-dependent chemical dynamics can be separated from those intrinsic to the molecule, (c) the effect of rotation of the reaction complex, and (d) the close relationship to polarization experiments, both LIF and chemiluminescence. We also calculate the J-dependent degree of alignment of electron density, and its dependence upon the electronic parity.

I. INTRODUCTION

The phenomenon of Λ doubling initially strikes many researchers in chemical dynamics as some obscure and minute spectroscopic effect, and it is true that the corresponding energetic splitting is normally completely negligible compared to other internal energies or to collision energies. However preferential population of one member of a Λ-doublet pair has been observed in chemical reactions, inelastic collisions, photodissociation, and surface scattering. The origin of this selectivity is the conservation of the orientation of a single electron $p\pi$ orbital as the nuclei move from a transition state to products via an approximately planar fragmentation. The orientation of that orbital within the transition state is normally well defined, regardless of whether it is nonbonding, antibonding, or bonding. In the diatomic $^2\Pi$ product molecules that we discuss here, *the relevant distinction between the two states* is neither their energetic splitting nor their total parity, it *is the difference of the direction of the orbitals relative to the molecular rotation plane*. It is precisely the unpaired orbitals which often have the most significant effect in heavy particle dynamics.

Observation of such preferential populations has been used to discuss the dynamics of chemical reactions,[1-8] and of rotational excitation.[9,10] Laser induced fluorescence (LIF) is usually used to identify the doublet states. However, there has been confusion about the basic interpretation of such experiments. From the results of our study of the photodissociation of H_2O,[11] and from subsequent theoretical work of Alexander and Dagdigian,[12] the main point of confusion has been resolved. In this paper we discuss the use of Λ doublets in product diatomics to analyze chemical reactions. We present qualitative and quantitative descriptions which should be useful in interpreting experimental results.

The primary reason that Λ doublets are of interest in particle dynamics is that, for large values of the total angular momentum J, there is an *unpaired $p\pi$* electron lobe in a rotating diatomic which lies perpendicular to the internuclear axis and is either (a) parallel to J or (b) in the plane of rotation (POR) of the molecule. The two Λ-doublet states are called π^+ and π^-, respectively, and represent these two different directions of the unpaired $p\pi$ electron lobe. (The $+$ and $-$ refer to the electronic parity P_e defined in the Appendix. The signs are reversed from those used by us in Ref. 11.) The confusion mentioned above was about which lobe direction corresponds to a given spectroscopic state, and accordingly, to a given probe-laser wavelength.

In a chemical reaction, e.g., the lobe might point toward the broken bond of which its electron was once a part. If the dissociation is planar and energetic, so that the bond has a spatial relationship to J, the results help to define the stereochemistry. For smaller values of J the degree of electron alignment is less, as described below.

QUALITATIVE DESCRIPTION OF $^2\Pi$ MOLECULES

Stationary nuclei

We discuss OH here, but with minor changes the discussion applies to other $^2\Pi$ molecules. Excellent descriptions[12-14] are available and we review only a few relevant points. The ground state is ... $(2p\sigma)^2(2p\pi)^3 \; ^2\Pi$, so that the component Λ of the orbital angular momentum of the single unpaired $p\pi$ electron along the internuclear axis (defined as the z axis) is $+1$ or -1. These two orbitals are degenerate and the different signs indicate opposite directions of current flow. This is analogous to the familiar case of $l = 1$, $m_l = \pm 1$ in the hydrogen atom, which is most often described by a linear combination of those two m_l states to yield two equal-density, stationary sets of electron lobes p_x and p_y, which are perpendicular to each other, but have an arbitrary angle about the z axis. Similarly, in stationary OH, the cylindrically symmetric electron distribution about the z axis can be described by two perpendicular sets of equal-density electron lobes.

There is also electron spin. In the $^2\Pi$ ground state the spin-orbit coupling aligns the spin with Λ, and yields two values for the z component of spin Σ of $1/2$ or $-1/2$. The electronic angular momentum is J and its z component $\Omega \, (= \Lambda + \Sigma)$, is $\pm 3/2$ or $\pm 1/2$, corresponding to the four possible combinations of Λ and Σ. The electronic energy of a multiplet term is approximately $T_0 + A\Lambda\Sigma$,[13] where A is the spin-orbit coupling constant, which can be positive or negative. Accordingly, the energy for $\Omega = |3/2|$ lies above or below, respectively, that for $\Omega = |1/2|$. For OH, A is negative.

Rotating nuclei

When the nuclei rotate, they produce a magnetic moment that increases with their angular momentum R, and that removes the degeneracy of $\Lambda = 1$ and -1, yielding two states, only one of which (the π^-) can interact with the first excited state ($^2\Sigma$) so that they separate in energy and produce the Λ doublets.

The magnetic field tends to decouple the electron spin from z [transition from Hund's case (a) to case (b)],[13] so that the situation in the stationary molecule, in which Λ and Σ were parallel or antiparallel, no longer applies. Instead, however, the wave functions can be written[9] as linear combinations of those wave functions Π_Ω (see the Appendix). These are

$$\psi_{1/2} = a_J \Pi_{1/2} + b_J \Pi_{3/2}$$

and

$$\psi_{3/2} = a_J \Pi_{3/2} - b_J \Pi_{1/2}, \tag{1}$$

where a_J and b_J are J dependent coefficients. Only states with the identical parity (see the Appendix) and J can mix. As the magnetic field increases with rotation, so does the inequality between the electron densities in the lobes corresponding to the Λ-doublet components.

Since rotational energy spacings are $\cong 2BJ$, where B is the rotational constant, and the spin-orbit energy is $\cong A$, there is no decoupling when $|A| \gg BJ$ and complete decoupling $(a_J = b_J)$ when $|A| \ll BJ$. It is reasonable to expect, and

is indeed true,[9,14] that the parameter $\lambda \equiv A /B$, will be important in discussing intermediate cases.

The extent to which the electron lobes are oriented is a strong function of λ, as was originally calculated by Gwinn et al.[8] and Bertojo et al.,[9] and was subsequently discussed by us.[11]

A measure of the inequality of the two lobes is Δ, which is equal to[8] $\langle \psi | x^2 - y^2 | \psi \rangle \propto \langle \psi | \cos^2 \phi - \sin^2 \phi | \psi \rangle$, where ϕ is the electron orientation about z, measured from x, and the POR is the xz plane. With cylindrical symmetry, $\Delta = 0$, while it is $\frac{1}{2}$ for fully oriented $p\pi$ lobes lying in the POR and $-\frac{1}{2}$ for those perpendicular to it. Calculations showed[8,9,11] (see the Appendix) that $|\Delta| = Sa_J b_J$ and that

$$Sa_J b_J = |\Delta|$$
$$= S\{4 + [\lambda - 2]^2/[(J-1/2)(J+3/2)]\}^{-1/2}, \tag{2}$$

where S is $[(J-1/2)/(J+3/2)]^{1/2}$,[12(a)] but was previously[8,9,11] taken to be unity. The following limiting cases apply: (a) as $J \to \infty$, $|\Delta| \to \frac{1}{2}$, which yields the two complete alignment cases, (b) as $|\lambda| \to \infty$, $\Delta \to 0$, with no alignment, (c) when $J = \frac{1}{2}$, $\Delta = 0$, there is no alignment, and (d) when $\lambda = 2$, $|\Delta| = \frac{1}{2}S$, which is approximately the case for CH. The sign of Δ is opposite that of the electronic parity P_e (see the Appendix). Of primary importance here is that at a given J, the orbital alignment strongly depends upon the particular molecule via λ, a ratio of molecular constants.

The ϕ dependence of the Λ-doublet wave functions may be written as

$$\psi = c_J \sin \phi + d_J \cos \phi \quad (\pi^+)$$

and

$$\psi = c_J \cos \phi - d_J \sin \phi \quad (\pi^-), \tag{3}$$

and the corresponding ϕ dependence of the electronic density ρ is

$$\rho = [c_J^2 \sin^2 \phi + d_J^2 \cos^2 \phi]/\sqrt{\pi} \quad (\pi^+)$$

and

$$\rho = [c_J^2 \cos^2 \phi + d_J^2 \sin^2 \phi]/\sqrt{\pi} \quad (\pi^-). \tag{4}$$

Equation (4) is derived in the Appendix and is shown schematically in Fig. 1.

It has been shown[9] that $c_J^2 = \frac{1}{2} + |\Delta|$, and $d_J^2 = 1 - c_J^2$, and together with Eq. (2) we can readily evaluate the extent to which the two electron lobes contribute.

An important consideration is the parity of the molecule (see the Appendix) because it determines selection rules governing electronic transitions. The two Λ-doublet components have different parities, which simplifies the measurement of their populations. In the $^2\Sigma \leftarrow {}^2\Pi$ transition that is
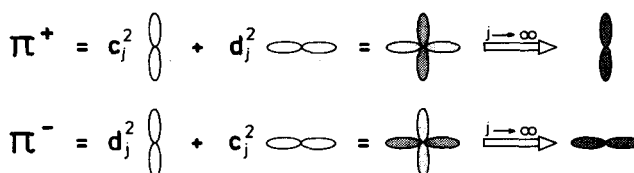

FIG. 1. Representation of the ϕ dependence of π^- and π^+ electron densities as a linear combination of pure $\sin^2 \phi$ and $\cos^2 \phi$ lobes, and perfect alignment as $J \to \infty$. Quantitatively, $c_J^2 = 1/2 + |\Delta|$, and $d_J^2 = 1/2 - |\Delta|$, where $|\Delta|$ can be calculated via Eq. (2).

usually used for LIF analyses, Q lines (i.e., $\Delta J = 0$) originate from π^+ states while P or R lines ($\Delta J = \pm 1$) originate from π^- states. This means that in spite of the very small energy splitting in Λ doublets, modest spectral resolution suffices to determine their relative populations by LIF methods. An energy level diagram, which includes parities, is in the Appendix.

DIRECTION OF LOBES

There was some doubt about the basic interpretation of reactions that produce unequal Λ-doublet populations. An example is the reaction $H + NO_2 \rightarrow NO + OH$, originally studied and analyzed by Mariella et al.[1-3] They measured a population ratio $PR \equiv \pi^-/\pi^+$ for the Λ-doublet states of $OH(^2\Pi)$. For large values of J, they stated that the physical difference between those two Λ-doublet components was the high-J electron-lobe orientations decribed in the Introduction. (These authors, as did we in Ref. 11, used the opposite $+$ and $-$ designations from those used here. This does not affect the lobe direction.)

They interpreted the reaction to proceed preferentially via a planar HONO complex, which decomposes to the products and thereby produces a POR for OH which lies in the HONO plane. This interpretation was supported by the Λ-doublet results, because the broken ON bond yields an unpaired $p\pi$ electron for OH (as well as one for NO), and so it tends to have that lobe primarily in the POR: i.e., a π^- state.

Murphy et al.,[6] obtained data for $D + NO_2$ similar to those of Mariella et al.,[1-3] but they challenged the interpretation. They relied upon the analysis of Gwinn et al.,[8] who concluded, from a moment of inertia argument, that the two states had lobes whose directions were just the reverse of those assigned by Mariella et al.

Our recent publication[11] contains three points which are relevant here. *The first point* is that the Mariella et al. assignment of the unpaired lobe orientations is correct, which lends credence to their interpretation of the dynamics. This result was later confirmed by Alexander and Dagdigian (AD),[12] and Kinsey[15] also agrees. We also show this result in the Appendix.

There is a $(p\pi)^3$ shell in OH, and we are discussing here the unpaired $p\pi$ lobe, not the filled $(p\pi)^2$. AD discuss instead the incomplete $(p\pi)^3$ shell. This is now a semantic point: We are in agreement with respect to the orientation of the unpaired orbital. Nevertheless, until recently the question whether the paired $(p\pi)^2$ lobe reversed the orientation of the unpaired lobe was controversial. It does not.

DEGREE OF ELECTRON ALIGNMENT

Our second point is that although Gwinn et al.[8] and Bertojo et al.[9] improperly reversed the lobe directions for the Λ-doublet states, they essentially correctly treated the behavior of the lobes at smaller J, where, as described above, they are less well oriented. [The factor S in Eq. (2) is a correction to their results.] Their equations agreed well with our experimental results for H_2O, and so we have confidence in using Eq. (2) to *determine whether any dependence of PR upon J is due to chemical dynamics or to incomplete lobe*
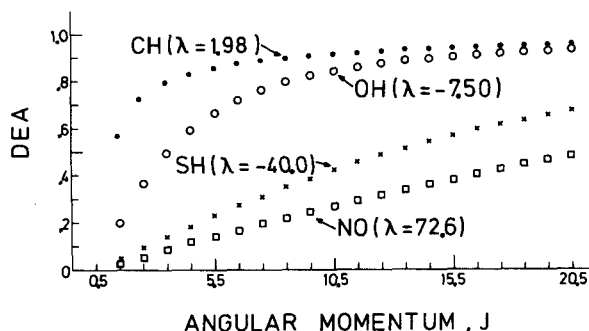
FIG. 2. The degree of electron alignment DEA $[\equiv(\pi^- - \pi^+)/(\pi^+ + \pi^-)]$ vs J, for four different $^2\Pi$ molecules with different values of λ, calculated from Eq. (5). This demonstrates that large differences in relative Λ-doublet populations for different molecules are to be expected, even at the same J, because of molecular properties alone, and this must be accounted for before the effects of chemical dynamics can be properly evaluated.

orientation for small J: i.e., to determine what small J means. This question is readily answered with the use of Eq. (2). The treatment is virtually the same as that in Ref. 11: The only differences are (a) the factor S and (b) that in the H_2O dissociation the pure case was that in which the $p\pi$ orbital was perpendicular to the POR, while in all the chemical reactions in Refs. 1–7, it is expected to lie in the POR. We find that $PR \equiv \pi^-/\pi^+ = c_J^2/(1 - c_J^2)$ and define a revised degree of electron alignment $DEA \equiv (\pi^- - \pi^+)/(\pi^+ + \pi^-)$, where the π are the populations of those states. The result is

$$DEA = S\{1 + [\lambda - 2]^2/[4(J - 1/2)(J + 3/2)]\}^{-1/2}, \quad (5)$$

where $\lambda \equiv A/B$. Full alignment implies $DEA = 1$. Values for DEA for four $^2\Pi$ species, calculated from Eq. (5), are shown in Fig. 2. The λ were obtained from the literature.[16] Note that $PR = (DEA + 1)/(1 - DEA)$. The degree of electron alignment is the physical quantity that determines the preferential Λ-doublet populations, not the energy splitting or the *total* parity.

For the previous example[1-3] $H + NO_2$, the data for OH are for J in the range 11.5–23.5. Figure 2 shows that $DEA = 0.83$ ($PR = 11$), at $J = 11.5$. In this range only a weak further J dependence of DEA is predicted and the two limiting lobe orientations are adequate for interpretation of this experiment. Within the limits of precision, the experimental PR is constant, which suggests that the dynamics are not J sensitive.

PLANARITY OF REACTION

Our third point concerns the effect of out-of-plane rotation of the transition state upon PR. We found[11] that with photodissociation from cold H_2O, the DEA for OH were essentially those shown in Fig. 2 (with the opposite sign). However, it was nearly zero with 300 K water. This temperature dependence showed that *an initial rotation of the transition state drastically reduced the Λ-doublet selectivity*. This effect is directly relevant here. If a planar complex is initially rotating out of its plane, the rotation will slow down and then stop as the complex dissociates, because the moment of inertia increases with internuclear distance. This yields a final plane which contains the POR of the fragment (and also the π^- lobe). Because overlap between the initial

lobe wave function and the final (π^-) wave function decreases with the angle between the initial and final planes, so does the PR.

Figure 3 shows a triatomic complex, rotating out-of-plane, in which an sp bound is to be broken and from which a $p\pi$ orbital is formed on the free diatomic. The case illustrated has the lobe at 45° to the original plane. As described in the figure caption, no Λ-doublet preference is expected. This model implies that with increasing dissociation velocity there will be less out-of-plane rotation and more Λ-doublet preference.

Consider the data obtained by Luntz[4] for the reaction $O(^1D) + H_2 \rightarrow OH + H$. Because three nuclei define a plane, the reaction is trivially planar. However, except for special trajectories, that plane rotates.

Calculations for this reaction are in excellent agreement with experimental determinations of rotational and vibrational distributions.[17] They indicate that the reaction proceeds by insertion of O into the H_2 bond. This produces H_2O in the electronic ground state, with a highly excited vibrational bending mode. The complex lives for several rotational periods, and in the dissociation the bending excitation is converted to OH rotation. Note that this dissociation is in-plane, and in the model presented above, is in competition with the out-of-plane rotation produced in the complex formation.

The experimental PR rises approximately linearly from 1.0 to 2.6 as J goes from 2.5 to 19.5. Figure 2 shows that at $J = 7.5$, where DEA = 0.76 and PR = 7, the electron lobes in OH are already reasonably well defined (our second point), and so this can not be a reason for either (a) the failure
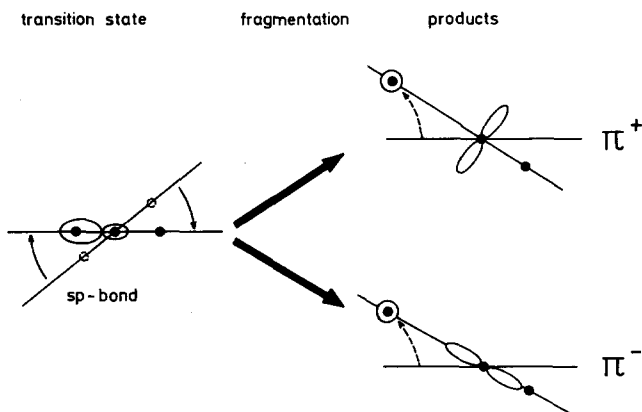
to approach the theoretical values for DEA or (b) the linear increase of PR with J, even for larger J.

Because an increasing J from an H_2O bending mode dissociation implies that the H–OH separation is more rapid, the final plane will be reached more quickly, and the angle between the initial and final planes will be less. This should yield an increase in PR with J_{OH}, in accord with the data.

An analogous measurement by Luntz[4] for the reaction of $O(^1D) + CH_4$ yielded smaller values for PR and a much slower rise with J. Because the moments of inertia of this complex are larger, out-of-plane rotation should have less effect here. Thus when the data, at large J, are compared for H_2 and CH_4, the smaller PR for the latter is most probably due to the nonplanarity of the reactions. Luntz measured still smaller PR for larger saturated alkanes.[4]

POLARIZATION EFFECTS

A different, but related method of measuring stereochemical effects is with polarized light either as (a) polarized LIF[11] or (b) polarization analysis of excited state fluorescence. Such methods have been analyzed, e.g., by Greene and Zare.[18] Rather than using the molecular coordinates exclusively, as is done in Λ doubling, a *laboratory* spatial anisotropy of J is created by some process, such as a chemical reaction or photodissociation. Measurement of the anisotropy involves the spatial relationship between the electric vector of the laser light and J in method (a) or the electric vector of the fluorescence and J in method (b), and in turn, that between J and the transition moment μ in both cases.

In a transition between a high-J $^2\Pi$ state, and the cylindrically symmetric $^2\Sigma$, μ clearly lies along the axis of the electron lobe. Figure 4 shows the case of a π^+ state at intermediate J. The higher-density lobe lies along J and does not rotate, the lower density lobe lies in the POR and rotates there with the molecule, and so the resultant density processes about J, as does μ. If we designate $\mu_\perp$ and $\mu_\parallel$ as the transition moments along the lobes perpendicular and parallel to the POR, respectively, it can be readily shown that $\mu^+ = c_J\mu_\perp + d_J\mu_\parallel$ (see Fig. 4), and that $\mu^- = c_J\mu_\perp - d_J\mu_\parallel$. Effects similar to those in Λ doubling appear. At high J, μ^+ would be along J and stationary. *At intermediate J,* as shown in Fig. 4, *it precesses* and therefore *has less anisotropy, even for perfect alignment* of J in the laboratory. In analogy with Fig. 2, it is clear that for equal J and equal alignment of J, we expect to see increasing polarization in the sequence NO, SH, OH, and CH. For a Hund's case (a)
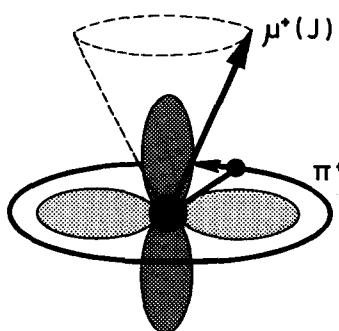

transition state   fragmentation   products

FIG. 3. Left: A triatomic bent transition state, with a rotating plane which is initially horizontal. One sp bond is also shown. Right: The sp bond breaks, leaving an s shell on the departing atom and a $p\pi$ lobe on the $^2\Pi$ diatomic, and the repulsion between the fragments provides a direction of nuclear rotation. As the fragments' separation becomes very large, we reach a final plane for the three atoms, here shown 45° from the original plane. The top and bottom figures indicate (high-J) π^+ and π^- states of the diatomic. For this angle it is clear that the overlap of wave functions with the original is identical in both situations and so no state preference is expected. As the angle of out-of-plane rotation decreases the π^- formation is increasingly preferred. If the diatomic has low J (not shown) then each of the lobes at the right would also have a weaker lobe perpendicular (in the plane of the paper) to it (See Fig. 1), and thus the preferential population of Λ-doublet states would be reduced. This implies that rapid breakup favors π^- because (a) the final plane is reached more quickly, and the out-of-plane rotation is less and (b) J will be greater.

FIG. 4. Direction of electron lobes, relative to rotating OH, at intermediate J and the resulting transition moment μ for a π^+ state. Because the lobe in the POR rotates with the molecule, so does its component of μ. As J increases and the fraction of the electron density in the lobe perpendicular to the POR becomes better oriented, the precession angle decreases and μ approaches J.

molecule like NO, at small J, there should be negligible polarization even with perfect molecular alignment.

The precessing dipoles should also lead to J-dependent polarization effects when molecules are born in a $^2\Sigma$ state and fluoresce back to the $^2\Pi$ ground state. This occurs in photodissociation processes (e.g., $H_2O \rightarrow OH^* + H$) as well as in chemiluminescent reactions. To our knowledge this effect has not been previously considered.

Another important J-dependent molecular effect is that caused by nuclear spins and is discussed in Refs. 18 and 19.

SUMMARY

In summary, in the analysis of reactions via Λ-doubling, the following factors are now established: (a) in the LIF example considered here ($^2\Pi \rightarrow {}^2\Sigma$ excitation) Q lines and P or R transitions originate from states in which the electron lobe is preferentially perpendicular to the molecular plane of rotation, or lies in it, respectively, (b) the degree to which these lobes are oriented depends strongly upon J, and upon the molecular parameter λ (the ratio of spin-orbit coupling constant to the rotational constant), and can be easily calculated via Eq. (5), so that the *J dependence of the chemical dynamics can be separated from those of the intrinsic molecular properties*, (c) out-of-plane rotations of the complex serve to reduce preferential Λ-doublet populations, so that the speed of the dissociation is important, and (d) these principles also apply to measurements of polarized fluorescence, whether laser induced or direct. While we discussed mainly chemical reactions here, these ideas can also be applied to inelastic collisions, photodissociation, rotational excitation, and surface scattering.

ACKNOWLEDGMENTS

APPENDIX. WAVE FUNCTIONS, PARITIES, AND LOBE ORIENTATION

The wave functions of OH in the coupling case intermediate to Hund's cases (a) and (b) are written[9] as an expansion of case (a) wave functions

$$\psi_{\Omega = 1/2, \epsilon, J} = a_J |^2\Pi_{1/2}^\epsilon\rangle + b_J |^2\Pi_{3/2}^\epsilon\rangle \tag{A1a}$$

and

$$\psi_{\Omega = 3/2, \epsilon, J} = -b_J |^2\Pi_{1/2}^\epsilon\rangle + a_J |^2\Pi_{3/2}^\epsilon\rangle, \tag{A1b}$$

where

$$a_J = \left[\frac{X - (\lambda - 2)}{2X}\right]^{1/2}, \tag{A2a}$$

$$b_J = \left[\frac{X + (\lambda - 2)}{2X}\right]^{1/2}, \tag{A2b}$$

$$\lambda \equiv A/B, \tag{A2c}$$

and

$$X \equiv [4(J + 1/2)^2 + \lambda (\lambda - 4)]^{1/2}, \tag{A2b}$$

and the case (a) wave functions[12] are

$$|^2\Pi_{1/2}^\epsilon\rangle = (4\pi)^{-1/2}[-e^{i\phi}\beta |JM\, 1/2\rangle + \epsilon e^{-i\phi}\alpha |JM - 1/2\rangle] \tag{A3a}$$

and

$$|^2\Pi_{3/2}^\epsilon\rangle = (4\pi)^{-1/2}[-e^{i\phi}\alpha |JM\, 3/2\rangle + \epsilon e^{-i\phi}\beta |JM - 3/2\rangle]. \tag{A3b}$$

The electronic angular momentum is taken into account by the eigenfunctions $-e^{+i\phi}$ and $+e^{-i\phi}$ of the angular momentum operator around the z axis. The electron spins α, β couple to the electronic angular momentum to give the projections $\Omega = \pm 1/2$ and $\Omega = \pm 3/2$. The $|JM\Omega\rangle$ are the symmetric top eigenfunctions which describe the nuclear rotation with a well defined projection Ω along the internuclear axis [Hund's case (a)]. The quantity ϵ relates to the total parity[20] by

$$P = \epsilon(-1)^{J - 1/2}. \tag{A4}$$

The two cases $\epsilon = \pm 1$ yield the two parity states (Λ-doublet states) for the same J.

The "true" OH wave function [Eq. (A1)] is described in terms of the Hund's case (a) wave functions. Only states with the same parity and the same J are mixed. The coefficients a_J and b_J were obtained from first order perturbation theory[9] and the results are listed in Eq. (A2).

The coordinate system is chosen to have (a) z as the internuclear axis, (b) the xz plane as the OH rotation plane, and (c) ϕ as zero along the x axis, i.e., for $\phi = 0°$ and $90°$ the orbitals are in the OH rotation plane or perpendicular to it, respectively. The out-of-plane lobe density thus corresponds to $(\sin^2 \phi)/\pi$ and that in-plane corresponds to $(\cos^2 \phi)/\pi$.

It is difficult to see the explicit ϕ dependence of the electronic density from Eqs. (A1) or (A3). In order to do this, the wave function is rewritten using the relation $\epsilon^{\pm i\phi} = \cos \phi \pm i \sin \phi$. This yields

$$\psi_{\Omega \epsilon J}(\tau, \phi) = ig^{-\epsilon}(\tau) \frac{\sin \phi}{\sqrt{\pi}} + g^\epsilon(\tau)\frac{\cos \phi}{\sqrt{\pi}} \tag{A5}$$

with the definitions

$$g^\mu(\tau) \equiv 1/2[-x\beta |JM\, 1/2\rangle + \mu x\alpha |JM - 1/2\rangle - y\alpha |JM\, 3/2\rangle + \mu y\beta |JM - 3/2\rangle] \tag{A6}$$

and

$$(x,y) \equiv \begin{matrix} (a_J, b_J) \\ (-b_J, a_J) \end{matrix} \quad \text{for} \quad \begin{matrix} \Omega = 1/2 \\ \Omega = 3/2 \end{matrix}. \tag{A7}$$

This yields the identical wave functions as given by Eqs. (A1) and (A3). τ represents all coordinates (including the electronic spin) except ϕ. The absolute value of $\psi_{\Omega J \epsilon}$ is obtained from

$$|\psi_{\Omega J \epsilon}|^2 = |g^{-\epsilon}|^2 \frac{\sin^2 \phi}{\pi} + |g^\epsilon|^2 \frac{\cos^2 \phi}{\pi}, \tag{A8}$$

and there is no $\sin \phi \cos \phi$ interference term.

This is integrated over τ, i.e., all coordinates but ϕ, to give the ϕ dependence of the electronic density ρ:

$$\rho_{\Omega J\epsilon}(\phi) = \frac{\sin^2\phi}{\pi}\int |g^{-\epsilon}|^2 d\tau + \frac{\cos^2\phi}{\pi}\int |g^\epsilon|^2 d\tau. \quad (A9)$$

The integration over τ is done analytically. After some algebra we obtain from Eq. (A6):

$$\int |g^\mu|^2 d\tau = 1/2 - \mu xyS, \quad (A10)$$

where

$$S = \langle JM - 1/2 | JM\, 3/2 \rangle. \quad (A11)$$

For the case $M = J$,

$$[(J - 1/2)/(J + 3/2)]^{1/2}, \quad (A12)$$

which yields

$$\rho_{\Omega J\epsilon}(\phi) = (1/2 + \epsilon xyS)\, 8 + (1/2 - \epsilon xyS)\infty, \quad (A13)$$

where the symbols 8, ∞ represent the out-of-plane and in-plane lobes, respectively. To discuss this ϕ dependence for the different quantum states we write the total parity as a product of the electronic and the rotational parity

$$P = P_e P_r. \quad (A14)$$

The rotational parity P_r is given by

$$P_r = (-1)^R, \quad (A15)$$

where R is the quantum number for the nuclear rotation ($R = 0,1,2,...$). Because $J = R + \Omega$, we find from Eq. (A4) that

$$\epsilon = \begin{array}{ll} P(-1)^{R+1} = -P_e & \text{for } \Omega = 3/2 \\ P(-1)^R = P_e & \Omega = 1/2 \end{array}. \quad (A16)$$

For the product xy we obtain from Eq. (A7):

$$xy = \begin{array}{ll} a_J b_J & \text{for } \Omega = 1/2 \\ -a_J b_J & \Omega = 3/2, \end{array} \quad (A17)$$

and from Eqs. (A16) and (A17) we obtain *for both $\Omega = 1/2$ and $\Omega = 3/2$:*

$$\epsilon xyS = P_e a_J b_J S. \quad (A18)$$

This yields the final result

$$\rho_{JP_e}(\phi) = (1/2 + P_e a_J b_J S)8 + (1/2 - P_e a_J b_J S)\infty, \quad (A19)$$

which is true for both $\Omega = 1/2$ and $\Omega = 3/2$. Equation (A19) is also illustrated in Fig. 1, where $(1/2 + P_e a_J b_J S)$ is c_J for $P_e = 1$ and d_J for $P_e = -1$. Obviously, the electronic density is distributed over both $p\pi$ lobes with the probability $1/2 + P_e a_J b_J S$ for the lobe out-of-plane and the probability $1/2 - P_e a_J b_J S$ for the in-plane lobe. *For $P_e = +1$ there is more electronic density in the out-of-plane lobe, while for $P_e = -1$ there is more for the in-plane lobe,* except for $J = 1/2$ where, via Eq. (A12), $S = 0$. This dominance of either the out-of-plane or the in-plane lobe is used to characterize the energy levels of OH in Fig. 5.

The electronic parity in Eq. (A19) is related to the total parity by

$$P_e = P(-1)^R. \quad (A20)$$

From Eqs. (2), (A19), and (A20), quantitative lobe orientation effects can be calculated for all J for both $\Omega = 3/2$ and $1/2$.

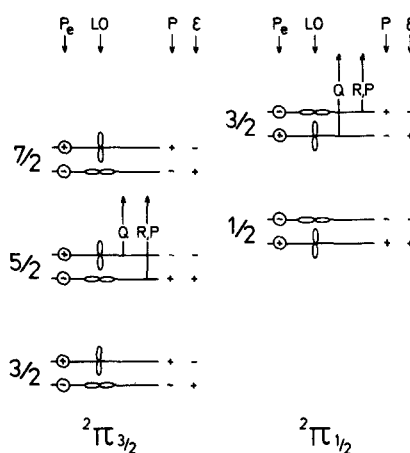From these equations it is straightforward to resolve the

FIG. 5. Schematic of an inverted (i.e., the spin-orbit constant A is negative) $^2\Pi_\Omega$ molecule. Shown are the index ϵ, the total and electronic parities P and P_e, and symbols which show the favored orientation of the electron lobes. For $J = 1/2$, there is *no* favored alignment, but it is shown so as to be consistent with the other members of the $^2\Pi_{1/2}$ manifold. Also shown are the levels which connect Q, or P,R lines with an upper $^2\Sigma$ state. Note that Q lines probe π^+ states, while P or R lines probe π^- states.

long controversy about the orientation of the unpaired electron in the upper Λ-doublet state for $\Omega = 3/2$. It was erroneously assumed[8] that the in-plane lobe corresponds to the upper Λ-doublet state. Consider the R with even values: for example for $R = 0$, $J = 3/2$ (see Fig. 5). It is known from spectroscopy that the upper Λ-doublet state has $P = 1$ and, from Eq. (A20), $P_e = 1$. From Eq. (A19) it is clear the out-of-plane lobe is preferred. Similar reasoning yields the other orientations shown in Fig. 5.

In previous theoretical work[8] these orientation effects were not used. Instead, the ϵ from Eqs. (A3) and (A5) were used and it was assumed that $\epsilon = +1$ corresponds to the upper Λ-doublet state for $\Omega = J = 3/2$. However, according to Eq. (A16), $\epsilon = +1$ implies $P_e = -1$, and thus $P = -1$. Thus $\epsilon = +1$ corresponds to the lower Λ-doublet state in which the lobe is more in-plane.

This erroneous interpretation of Λ-doublet states led to incorrect pumping theories of astronomical OH masers.

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