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Conical Intersections of Three Electronic States Affect the Ground State of Radical Species with Little or No Symmetry: Pyrazolyl

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We consider the seemingly arcane matter of accidental conical intersections of three states of the same symmetry.^{1,2} Whereas conical intersections of two states of the same symmetry, two-state intersections, are well-known, three-state conical intersections have been largely ignored. Here, we establish the importance of considering this class of conical intersection, reporting for the first time an accidental three-state conical intersection that will significantly modify the ground-state vibrational spectrum of the organic radical pyrazolyl, (CH)₃N₂. Further, our analysis of this intersection suggests an entire class of molecules likely to exhibit this type of three-state conical intersection.

An equilibrium geometry, a local minimum, on the ground-state potential energy surface (PES) is, in the absence of conical intersections, an isolated feature. However, if a two-state conical intersection, involving the ground-state PES and the first excited PES, exists in this region, then instead of a single isolated minimum there are a series of local extrema that are coupled by motion along two internal vibrational modes. If the conical intersection involves three states, the number of extrema and internal coupling modes increases. For example, the three-state, five vibrational mode, T × (e, t₂) Jahn–Teller problem can have 13 local extrema coupled by motion along five vibrational coordinates,³ producing a very complicated spectrum. A conical intersection also affects nuclear motion on the excited PES where it produces a funnel that routes the molecule toward the intersection, thereby facilitating a nonadiabatic transition.

Given the potential impact of conical intersections, anticipating their existence is key. Conical intersections are conventionally associated with point group symmetry, which either requires (in the case of a multidimensional irreducible representation), or allows (for states of different symmetry), the intersection. However, this conventional association is misleading because the noncrossing rule⁴ demonstrates that symmetry is not essential for a conical intersection. Indeed, in the past decade, it has become clear that two-state conical intersections for which symmetry is irrelevant are ubiquitous and play an essential role in electronically nonadiabatic processes. Three-state intersections were largely ignored in this period. This neglect stems from the fact that, when compared to two-state conical intersections, three-state intersections are quite rare. To quantify this statement, note that conical intersections are not, in general, isolated points but are continuously connected subspaces, lines, surfaces, or volumes, etc., in the higher dimensional nuclear coordinate space. According to the noncrossing rule⁴ for *n*-state conical intersections, these subspaces have dimension $N^{\text{int}} - 2$ [$N^{\text{int}} - 5$] for *n* = 2 [3], where N^{int} is the number of internal coordinates. To see what this means, assume $N^{\text{int}} - 2 = 3$ so that the two-state conical intersection points fill a volume. Then, because a three-state conical intersection is also two-state conical intersection, that volume would contain only the single three-state conical intersection point.

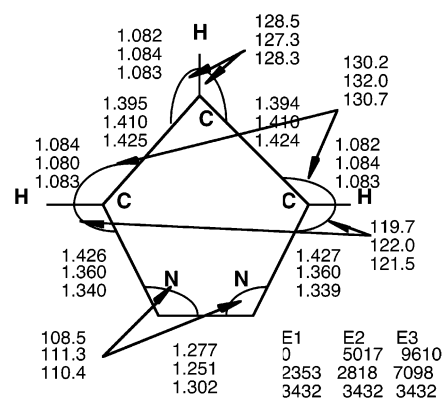


Figure 1. Pyrazolyl using CI2 wave functions. Each column of triples gives a quantity evaluated at $1^2A''(\text{min})$ [top], $1^2A'(\text{min})$ [middle], $1,2,3^2A(\text{mex})$ [bottom], respectively. Bond distances (Å) are placed adjacent to indicated bonds, angles (deg) are indicated by arrows, and energies (cm^{-1}) are under columns labeled E1, E2, and E3.

While this dimensional argument may appear compelling, recent work indicates that ignoring three-state intersections may be ill-advised. Three-state conical intersections have been found in the ethyl¹ and allyl² radicals, extending to the realm of large-scale multireference configuration interaction wave functions, earlier work that identified accidental three-state intersections in CH_4^+ using Frost functions.⁵ The three-state intersections in the ethyl and allyl studies involved exclusively excited electronic states. We are not aware of any molecules where a low-lying, accidental, three-state conical intersection involving the ground electronic state has been located on the basis of reliable ab initio wave functions. Here, we show that pyrazolyl, and, by extension, a whole class of molecules, have a low-lying seam of three-state conical intersections. Pyrazolyl is being studied experimentally in Lineberger's laboratory.⁶ Interest in this radical is due, in part, to the general interest in polynitrogen compounds as potential high performance rocket fuels.⁶ The vibrational spectrum of this pyrazolyl is quite complex.⁶ We will demonstrate that this complexity is likely due to accidental three-state conical intersections near the ground-state minimum.

We begin with a qualitative model, which will prove useful when considering the generality of this type of three-state conical intersection. Pyrazolyl is a planar five-member ring with two adjacent nitrogens, see Figure 1. Its five π orbitals, $2p_z$ orbitals from the sp^2 hybridized carbons and nitrogens, hold five electrons. To describe the low-lying electronic states, we ignore (temporarily) the distinction between N and CH and use C_{5v} symmetry labels, in which case the five π orbitals carry a_1 , e_1 , and e_2 irreducible representations. Considering only the π -space, the three low-lying electronic states arise from the following wave functions: $\Psi_1 = a_1^2 e_{1x} e_{1y}$, $\Psi_2 = a_1^2 e_{1x} e_{1y}^2$, $\Psi_3 = a_1 e_{1x}^2 e_{1y}^2$. Note that Ψ_3 is $a_1 \rightarrow e_1$ excitation from Ψ_1 or Ψ_2 . In C_{5v} symmetry, (Ψ_1, Ψ_2) [Ψ_3] carry an 2E_1 [2A_1] irreducible representation. This is quite similar to the

situation in H_3 , where these three wave functions, with e replacing e_1^3 , and $e_x^2 + e_y^2$ replacing e_1^4 , give rise to a well-known three-state intersection, an accidental intersection of a doubly degenerate 2E state and a 2A_1 state, obtained by varying the symmetric stretch coordinate with the molecule constrained to D_{3h} structures. In this (2,1)-paradigm (for two quasi degenerate states and one singly excited state), the accidental three-state intersections are quite high in energy, attributable, at least in part, to the stability of the a_1 orbital.

In pyrazolyl, this (2,1)-paradigm is modified in an essential manner by the availability of a nonbonding orbital constructed from the nitrogen lone pair orbitals. The Ψ_i become the following: $\Psi_1 = a_1^2 \sigma_{lp}^2 e_{1x}^2 e_{1y}$, $\Psi_2 = a_1^2 \sigma_{lp}^2 e_{1x} e_{1y}^2$, while $\Psi_3 = a_1^2 \sigma_{lp} e_{1x}^2 e_{1y}^2$. Here, σ_{lp} is a delocalized combination of nitrogen nonbonding orbitals. While $\tilde{\Psi}_1$ and $\tilde{\Psi}_2$ are largely unchanged, $\tilde{\Psi}_3$ changes qualitatively to Ψ_3 , which is expected to contribute at lower energies because it involves a $\sigma_{lp} \rightarrow \pi$ excitation, avoiding excitation from a more stable bonding orbital. Thus, the availability of σ_{lp} gives rise to low energy three-state conical intersections. We refer to this as the (2,1_{lp})-paradigm.

The quantitative description of the states in question is based on multireference configuration interaction (MRCI) wave functions comprised of up to 40 million configuration state functions (CSFs). Using standard Dunning polarized Gaussian double- ζ basis sets, cc-pvdz, for all atoms, molecular orbitals were obtained from a state-averaged complete active space self-consistent field calculation of the three lowest states. The active space includes the two nitrogen lone pairs and all five π orbitals. Two MRCI expansions based on this active space were used: CII consisting of the active space CSFs plus all singly excited CSFs ($\sim 700\,000$ CSFs), and CI2 (restricted to C_s symmetry, see below) consisting of CII plus all double excitations with the interacting space restriction (~ 40 million CSFs in each of A' and A'' symmetry). CII, which had no spatial symmetry restrictions, was used for the preliminary characterization of the 1,2,3 2A states, while CI2 was used to obtain more reliable energies. Energies are reported relative to the lowest energy minimum of the ground electronic state, $E_1(1^2A(\text{min})) = -224.384193$ (-224.803920) au using CII(CI2).

The ab initio calculations confirmed the following aspects of the (2,1_{lp})-paradigm: (i) The π -space consists of delocalized orbitals involving both carbon and nitrogen. (ii) Ψ_3 rather than $\tilde{\Psi}_3$ is involved in the description of the lowest three states, the 1,2,3 2A states. (iii) For planar geometries, the 1,2,3 2A states are the 1,2 ${}^2A''$ and 1 ${}^2A'$ states.

A three-state conical intersection will give rise to multiple minima on the ground-state PES. While it is beyond the scope of this work to find all such minima, we did establish the existence of two proximal local coplanar minima on the ground-state PES using CII. Using CI2, Figure 1 reports the geometry and energies of these

two minima, where 1 ${}^2A''(\text{min})$ [1 ${}^2A'(\text{min})$] is a minimum of the 1 ${}^2A''$ [1 ${}^2A'$] state. We were unable to locate a local minimum for either the 2 2A or the 3 2A states in this region. This failure is consistent with the existence of a two-state conical intersection seam connecting the 3,2 2A states and a second seam connecting the 2,1 2A states.

The limited separation⁶ of the 1,2,3 2A states at 1 ${}^2A''(\text{min})$ and 1 ${}^2A'(\text{min})$ evident in Figure 1 suggests the existence of a three-state conical intersection.² At the CII level, an energy optimized three-state conical intersection with a coplanar structure was located, using an analytic gradient driven algorithm.¹ From this structure a three-state conical intersection, denoted 1,2,3 ${}^2A(\text{mex})$, was located using CI2 and is described in Figure 1. There it is seen that the three-state intersection is only 3432[1079] cm^{-1} above the lowest [secondary] energy minimum on the ground-state PES. These results support the (2,1_{lp})-paradigm.

The three-state intersection determined using CII, with $R(\text{C}-\text{C}) = 1.415$ Å, $R(\text{C}-\text{N}) = 1.359$ Å, and $R(\text{N}-\text{N}) = 1.357$ Å, is geometrically similar to 1,2,3 ${}^2A(\text{mex})$, although the degenerate energy is 4628 cm^{-1} . The fact that a three-state conical intersection is observed for both CII and CI2 provides strong evidence that this result is not an artifact of the computational approach. 1,2,3 ${}^2A(\text{mex})$ (and 1 ${}^2A''(\text{min})$, 1 ${}^2A'(\text{min})$) has (each have) approximately C_{2v} symmetry, although that was not a constraint of the calculation. For 1,2,3 ${}^2A(\text{mex})$, this approximate symmetry is attributed to the energy minimization part of the search algorithm. The fact that the three states are degenerate to less than 1 cm^{-1} although the symmetry is not exactly C_{2v} reflects the fact that symmetry is not a prerequisite for an intersection to exist.⁴

The presents calculations suggest that a doublet radical will have low-lying three-state conical intersections provided (i) there exists a low-lying LUMO and (ii) the highest doubly occupied molecular orbital is a nonbonding, lone pair, or similar orbital. Because molecules with low-lying three-state conical intersections are not expected to be rare, it is perhaps time to revisit the spectroscopy of such molecules, without the simplifications of a symmetry-required intersection.

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