Symmetry Friend or Foe: Confluences of Conical Intersection Seams in Tetra-Atomic Molecules†

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It is usually assumed that seams of conical intersection are isolated features, that is, a displacement perpendicular to the seam leads to a removal of the degeneracy. However, this need not be the case. It has been shown that for triatomic molecules, there may exist a confluence of an accidental symmetry-allowed C_{2v} seam of conical intersection with an accidental C_s seam of conical intersection of two states of the same symmetry. Here, we demonstrate the existence of a related confluence of seams of conical intersection in the tetra-atomic molecule isocyanic acid. Such confluences have not been previously reported. A perturbative analysis of the vicinity a seam of conical intersection is used to explain origin of this novel locus of conical intersection points.

I. Introduction

Points of conical intersection are continuously connected, forming seams. The seam is a surface of dimension $N^{\text{int}} - 2$, where N^{int} is the number of internal coordinates.[1] Perpendicular to the seam is a plane, the g−h[2] or branching[3] plane, in which the energy has the form of a double cone, that is, the degeneracy is lifted in a linear manner. Because the dimension of the seam plus that of the g−h plane is N^{int} seams are expected to be isolated features, where isolated implies that there exists a volume that contains this and only this seam. Recently, it was shown that this is not always the case in triatomic molecules.[4−7] In some triatomic molecules, all of which had C_{2v} or higher symmetry, an intersection or confluence of a symmetry-allowed seam of conical intersection, and a seam of conical intersection of two states of the same-symmetry (a same-symmetry seam) was found. We showed how these confluences could be anticipated using the cross product of the two vectors that define the g−h plane.[8,9] Subsequently, intersections of three symmetry equivalent, symmetry-allowed seams, with one symmetry-required seam were found in X_3 molecules.[10,11]

In a triatomic molecule, the seams are lines so that identifying the two seams that form the intersection is straightforward. The situation is more complex in molecules with more than three atoms. Here, the seam is a generalized line of dimension $N^{\text{int}} - 2 \geq 4$. Thus, it is not possible to say by inspection whether a pair of adjacent points of conical intersection belong to the same or distinct seams of conical intersection. Here, we will refer these distinct seams as distinct branches of an overall seam to emphasize the fact that the same two electronic states are involved throughout.

In this work, a previously reported[12] perturbative description of the vicinity of a point of conical intersection is used analyze the symmetry-allowed seam of conical intersection between an A′ and an A″ state in a tetra-atomic molecule. It is shown for this symmetry-allowed seam of conical intersection a confluence with a same-symmetry seam is possible. Criteria for identifying points on the distinct branches of the seam of conical intersection are established. Several interesting aspects of the analysis reflect the fact that a coplanar arrangement of four atoms has only one totally nonsymmetric mode in C_s symmetry.

In Section II, perturbation theory is used to develop criteria for identifying points on distinct branches of a seam of conical intersection near their confluence. In Section III, these criteria are used to demonstrate the existence of intersecting branches for the S_1-S_0 seam of conical intersection in HNCO. The identification of this confluence is particularly timely as radiationless decay of the $S_1[1^1A''(2^1A)]$ state of HNCO, which is attributable to the S_1-S_0, seam of conical intersection, has recently been a topic of considerable interest.[13−17] Section IV provides a summary and our conclusions.

II. Theory

The adiabatic states $\Psi^a(\mathbf{r};\mathbf{R})$ eigenfunctions of the electronic Schrödinger equation

$$[H(\mathbf{r};\mathbf{R}) - E_{\text{K}}(\tau)]\Psi^a_K(\mathbf{r};\mathbf{R}) = 0 \tag{1}$$

may be expressed in a basis of symmetry-adapted configuration state functions (CSFs, ψ)[18] as

$$\Psi^a_{\text{K}}(\mathbf{r};\mathbf{R}) = \sum_{\alpha=1}^{N^{\text{CSF}}} c^K_\alpha(\tau)\psi_\alpha(\mathbf{r};\mathbf{R}) \tag{2a}$$

so that the $\mathbf{c}^{\text{K}}$ satisfy

$$[\boldsymbol{H}(\tau) - E_{\text{K}}(\tau)]\mathbf{c}^K(\tau) = 0 \tag{2b}$$

Here, $\mathbf{r}$ denotes the $3N^{\text{el}}$ electronic coordinates, $\mathbf{R}$ denotes the $3N^{\text{nuc}}$ space-fixed nuclear coordinates, and τ denotes N^{int} intersection adapted internal nuclear coordinates.[3] Intersection adapted coordinates are a set of generalized cylindrical polar coordinates with origin τ_x, a point of conical intersection of states I and J, and (x,y)-plane given by the branching[3] or g−h[2] plane which is spanned by the tuning mode[19] $\mathbf{x} = \mathbf{g}^{\text{IJ}}/g$, and the coupling mode $\mathbf{y} = \mathbf{h}^{\text{IJ}}/h$, where $g = ||\boldsymbol{g}^{\text{IJ}}||$, $h = ||\boldsymbol{h}^{\text{IJ}}||$, and

$$2g^{IJ}_\tau(\tau) = -\mathbf{c}^I(\tau_x)^\dagger\frac{\partial \boldsymbol{H}(\tau)}{\partial\tau}\mathbf{c}^I(\tau_x) + \mathbf{c}^J(\tau_x)\frac{\partial \boldsymbol{H}(\tau)}{\partial\tau}\mathbf{c}^J(\tau_x) \tag{3a}$$

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$$h_\tau^{IJ}(\tau) = \mathbf{c}^I(\tau_x)^\dagger \frac{\partial \boldsymbol{H}(\tau)}{\partial \tau} \mathbf{c}^J(\tau_x) \tag{3b}$$

The remaining $N^{\text{int}} - 2$ mutually orthogonal internal coordinates, $\mathbf{z}^i$, $i = 1 - (\text{N}^{\text{int}} - 2)$, describe the seam. In these coordinates, $\boldsymbol{H}^{\text{d},(2)}(\tau)$, the electronic Hamiltonian for states I and J through second order in the displacement from τ_{x} is given by

$$\boldsymbol{H}^{\text{d},(2)}(\tau) = \Sigma^{(2)}(\tau)\boldsymbol{I} + [-gx + A(\tau)]\,\sigma_{\text{z}} + [hy + B(\tau)]\sigma_x \tag{4}$$

where σ_x, σ_y, σ_z are the Pauli spin-matrices

$$\Sigma^{(2)}(\tau) = s_x x + s_y y + \sum_i s_{z^i} z^i + N(\tau) \tag{5a}$$

$$s_\tau^{IJ}(\tau) = \mathbf{c}^I(\tau_x)^\dagger \frac{\partial \boldsymbol{H}(\tau)}{\partial \tau} \mathbf{c}^I(\tau_x) + \mathbf{c}^J(\tau_x) \frac{\partial \boldsymbol{H}(\tau)}{\partial \tau} \mathbf{c}^J(\tau_x) \tag{5b}$$

and

$$A(\tau) = (a_1^{(\rho)}x^2 + a_2^{(\rho)}y^2 + a_3^{(\rho)}xy) + \sum_i (a_1^{(z_i)}xz_i + a_2^{(z_i)}yz_i) \tag{6a}$$

$$\equiv \rho^2 A^{(\rho)}(\theta) + \rho \sum_i z_i A^{(z_i)}(\theta)$$

$$B(\tau) = (b_1^{(\rho)}x^2 + b_2^{(\rho)}y^2 + b_3^{(\rho)}xy) + \sum_i (b_1^{(z_i)}xz_i + b_2^{(z_i)}yz_i) \tag{6b}$$

$$\equiv \rho^2 \text{B}^{(\rho)}(\theta) + \rho \sum_i z_i B^{(z_i)}(\theta)$$

$$N(\tau) = (n_1^{(\rho)}x^2 + n_2^{(\rho)}y^2 + n_3^{(\rho)}xy) + \sum_i (n_1^{(z_i)}xz_i + n_2^{(z_i)}yz_i) + \sum_{i,j} n_3^{(z_i z_j)} z_i z_j \tag{6c}$$

$$\equiv \rho^2 \text{N}^{(\rho)}(\theta) + \rho \sum_i z_i N^{(z_i)}(\theta) + \text{N}^{(\text{z,z})}$$

The second-order contributions $A(\tau)$, $B(\tau)$, and $N(\tau)$ are the most general form consistent with a piecewise linear representation of the seam. With the exception of $n_i^{(w)}$, these coefficients can be determined from the circulation, the line integral[20] along a closed loop, of the derivative coupling.[12]

For this $^1\text{A}' - {}^1\text{A}''$ seam of conical intersection, we can, without loss of generality, require $\mathbf{x} \sim a'$ and $\mathbf{y} \sim a''$, where $\sim$ means "transforms as". This symmetry requires some of the above constants to vanish so that

$$\text{A}(\tau) = (a_1^{(\rho)}x^2 + a_2^{(\rho)}y^2) + \sum_i a_1^{(z_i)}xz_i \tag{7a}$$

$$B(\tau) = b_3^{(\rho)}xy + \sum_i b_2^{(z_i)}yz_i \tag{7b}$$

As a consequence of these symmetry-imposed constraints and the fact that there is only one a'' mode, $H_{IJ}^{(2),\text{d}} = hy + B(\tau)$ is factorable, $H_{IJ}^{(2),\text{d}} = H^i H^{ii}$ where

$$H^{\text{i}}(x,y,\boldsymbol{z}) = y \tag{8ai}$$

$$H^{\text{ii}}(x,y,z) = h + b_3^{(\rho)}x + \sum_i b_2^{(z_i)}z_i \tag{8aii}$$

This factorization is key. As a result of the factorization, the conditions for a seam of intersection $H_{IJ}^{(2),\text{d}} = G = 0$, where

$$G(x,y,z) = (a_1^{(\rho)}x^2 + a_2^{(\rho)}y^2) + \sum_i a_1^{(z_i)}xz_i - gx \tag{8b}$$

yields *two* pair of equations, that is, the seam consists of two branches, $S(i)$ and $S(ii)$ where points on $S(i)$ satisfy $H^i = G = 0$ and those on S(ii) satisfy $H^{ii} = G = 0$.

$S(i)$ is confined to the subspace $y = 0$, the C_s symmetry subspace. Therefore, any nonplanar τ_x necessarily belongs to $S(ii)$. From eq 4, the coupling mode for $S(i)$ is perpendicular to the molecular (y = 0) plane, so that it has a'' symmetry. Thus, $S(i)$ represents a symmetry-allowed seam of two states of different symmetry. $S(ii)$, on the other hand, is not confined to the space $y = 0$. It can exist for non planar geometries, where it necessarily constitutes a same symmetry intersection. The observations in this paragraph provide a criterion (criterion I) for determining points on $S(ii)$.

The seam equations, $H^{ii} = G = 0$ and $H^i = G = 0$ can be solved to find the locus of points of confluence of conical intersections. Because $G = 0$ is common to both seams, the solution space for the confluence has dimension $N^{\text{int}} - 3$. The confluence, if it exists, occurs for $y = 0$, that is, for planar geometries. The point (x, 0, z) lies at a confluence provided

$$-(h + \sum_i b_2^{(z_i)}z_i)/b_3^{(\rho)} = x \tag{9a}$$

$$x[(a_1^{(\rho)}x) + (-g + \sum_i a_1^{(z_i)}z_i)] = 0 \tag{9b}$$

In this work, we do not solve eq 9a and 9b to locate a confluence, using instead a procedure based on knowledge of $\mathbf{g}^{\text{IJ}} \times \mathbf{h}^{IJ}$. See Section III and Refs 8 and 21.

Equation 8, parts a and b, can also be used to construct ∇G and $\nabla H_{IJ}^{(2),\text{d}}$ for seam $S(i)$ and seam $S(ii)$

$$\nabla G = (-g + a_1^{(\rho)}x + \sum_i a_1^{(z_i)}z_i)\,\boldsymbol{i},\ 2a_2^{(\rho)}y\,\boldsymbol{j},\ a_1^{(z_i)}x\,\boldsymbol{k}_i \tag{10a}$$

$$\nabla H^i = \boldsymbol{j} \qquad \nabla H^{ii} = b_3^{(\rho)}\,\boldsymbol{i},\ 0\,\boldsymbol{j},\ b_2^{(z_i)}\,\boldsymbol{k}_i \tag{10b}$$

From eq 10b, the vectors ∇H^ι, ∇H^u are seen to be orthogonal.[22] This then is a criterion (criterion II) for identifying points belonging to distinct branches of a seam of conical intersection in the neighborhood of their confluence. Noting that for wave functions, given by eq 2, $\nabla G \rightarrow \mathbf{g}^{IJ}$ and $\nabla H_{IJ}^{(2),\text{d}} \rightarrow \mathbf{h}^{IJ}$, and that these directions are orthogonal to the $\mathbf{z}^i$, the seam coordinates, this criterion can be rephrased as

Two adjacent points $\tau_x(k)$, $k = i,j$, of conical intersection are associated with distinct branches of a seam of conical intersection provided either $\mathbf{g}^{IJ}(\tau_x(i))$ or $\mathbf{h}^{IJ}(\tau_x(i))$ can be expanded in terms of $\mathbf{z}^i(\tau_x(j))$, the seam directions for $\tau_x(j)$

This criterion will be applicable to analogous confluences in molecules with more than four atoms, for which, however, factorization of $H_{IJ}^{(2),\text{d}}$ cannot be guaranteed. Confluences of seams of conical intersection have not been reported for tetra-atomic molecules. Below, the existence of a confluence of this type is demonstrated in HNCO.

III. Intersection Seams of Conical Intersection in HNCO

The excited S_1 state of HNCO has both cis and trans minima, although only the trans minimum has been observed. Following photoexcitation from S_0, HNCO in S_1 can decay to ground-state H + NCO. Direct decay on S_1 is precluded by a large

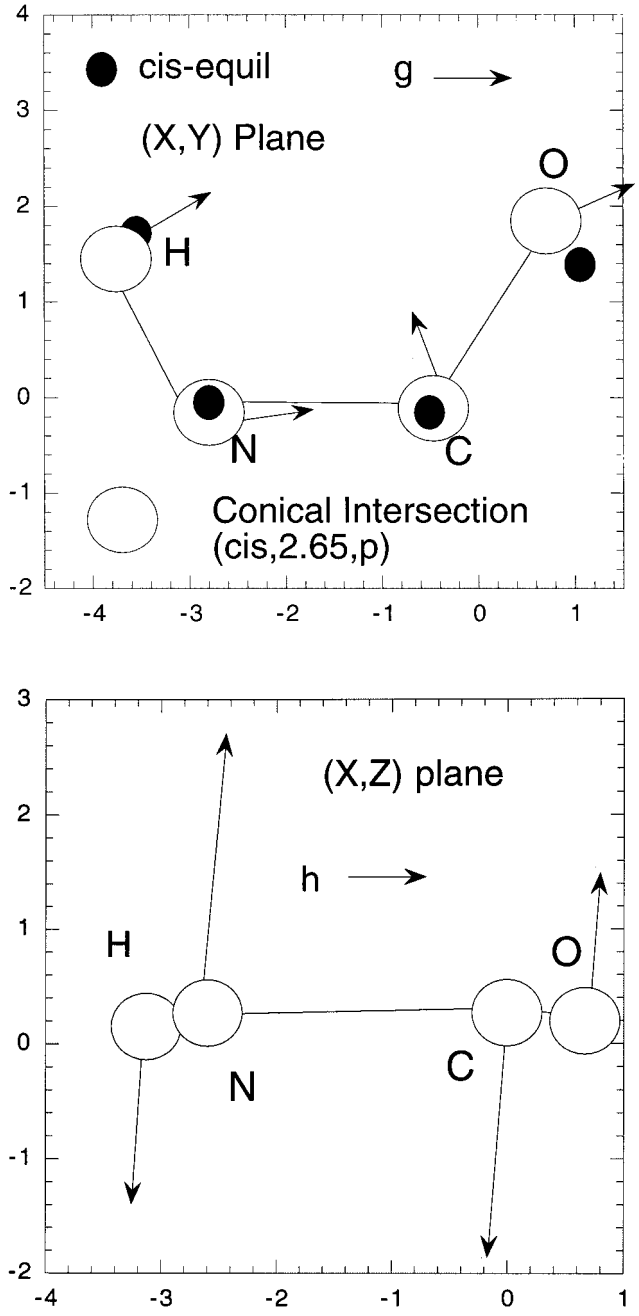

Figure 1. (a) In the molecular (X,Y) plane:τ_{eq}(cis) filled circles; τ_x(cis, 2.65,p) open circles and scaled $\mathbf{g}^{IJ}$ filled arrows. (b) In the (X,Z) plane scaled $\mathbf{h}^{IJ}$ filled arrows.

barrier, necessitating a radiationless transition to S_0 prior to dissociation.[15,16] To describe this nonadiabatic transition, we have previously determined the portions of the $S_1 - S_0$ ($1^1A - 2^1A$) seam of conical intersection for both cis and trans arrangements of HNCO as a function of R(C−N) using a large (approximately 3.5 million) CSF expansion.[23] Both planar and nonplanar structures were found. These points of conical intersection were denoted τ_x(w,R(C−N),z) where w = cis or trans, and z = planar(p) or nonplanar (np). For the planar, C_s, geometries encountered in that study, the ground and excited states are of $^1A'$ and $^1A''$ symmetry, respectively. In this case $\mathbf{g}^{IJ}$ [$\mathbf{h}^{IJ}$] has a' [a''] symmetry.

Figure 1a and 1b depicts τ_x(cis, 2.65, p) the planar (all atoms in the (X,Y) plane) point of conical intersection with R(C−N) = 2.65 a_0 together with the corresponding $\mathbf{g}^{IJ}$ and $\mathbf{h}^{IJ}$. Note that $\mathbf{g}^{IJ}$ is in the molecular (X,Y) plane, whereas $\mathbf{h}^{IJ}$ is perpendicular

TABLE 1: Points on Two Intersecting Branches of $1^1A - 2^1A$ Seam of Conical Intersection[a]

R(C−N)	R(N−H)	R(CO)	∠HNC	∠NCO	∠HNCO	E
		$S(ii)$:same symmetry branch				
2.66	1.944	2.288	103.4	105.9	−2.4	5952.1
2.67	1.955	2.271	103.7	106.1	−3.9	5946.5
		$S(i)$:symmetry allowed branch				
2.65	1.940	2.375	111.2	109.4	0	4529.3

[a] Energies in cm^{-1} relative to the energy at τ_{eq}(cis), $E^1A'' = -168.098\,267$ au.

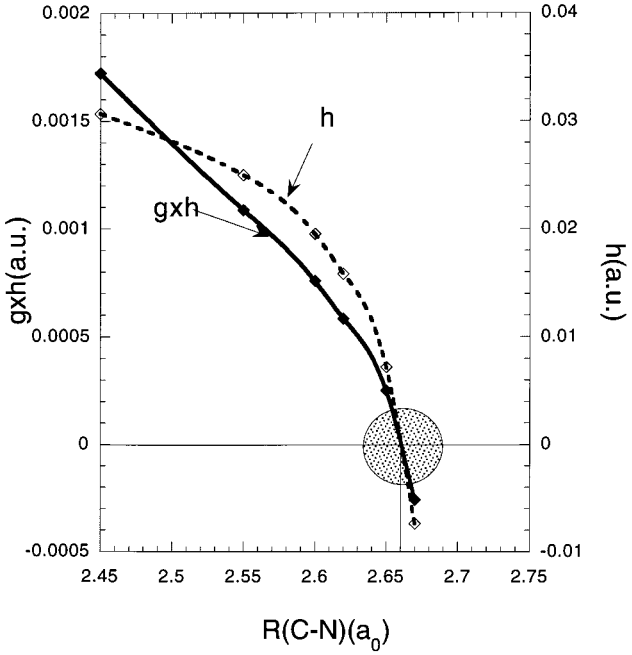

Figure 2. $\mathbf{g}^{IJ} \times \mathbf{h}^{IJ} \equiv gh\sin\alpha$, where α is the included angle, and h is plotted vs R(C−N). The vanishing of h indicates an intersection of branches of a seam of conical intersection.

to that plane, that is, they have a' and a'' symmetry, respectively, as expected. To demonstrate that the points of conical intersection considered here do not occur in an irrelevant region of nuclear coordinate space, Figure 1a compares τ_x(cis, 2.65, p) with the cis- equilibrium structure on S_1, τ_{eq}(cis) and Table 1 reports the relevant energies.

Figure 2 plots $\mathbf{g}^{IJ} \times \mathbf{h}^{IJ}$ and h for τ_x(cis, R(C−N), np) as a function of R(C−N), for R(C−N) near 2.65 a_0. From this plot, it is seen that $\mathbf{g}^{IJ} \times \mathbf{h}^{IJ}$ and h vanish near R(C−N) = 2.65 a_0. This suggests a confluence of two branches of the $1^1A - 2^1A$ seam of conical intersection in this region. According to the results of Section II, the confluence should consist of the symmetry-allowed $1^1A' - 1^1A''$ branch and a same-symmetry $1^1A - 2^1A$ branch. For near C_s geometries on the same symmetry branch, the coupling mode $\mathbf{h}^{IJ}$ is predicted to have, approximately because the molecule is not planar, a' symmetry, a highly counterintuitive result, given the proximity of the $^1A' - {}^1A''$ conical intersection, where $\mathbf{h}^{IJ} \sim a''$. This point is considered in Figure 3 which reports $\mathbf{g}^{IJ}$ and $\mathbf{h}^{IJ}$ for the slightly nonplanar point of conical intersection τ_x(cis,2.66,np). See Table 1. From Figure 3, both $\mathbf{g}^{IJ}$ and $\mathbf{h}^{IJ}$ are seen to be approximately contained in the "molecular plane", that is, again in an approximate sense, both $\mathbf{g}^{IJ}$ and $\mathbf{h}^{IJ}$ are of a' symmetry! Thus, $\mathbf{h}^{IJ}(\tau_x$(cis,2.66,np)) is contained in the seam space of τ_x(cis,2.65,p), and the converse is also true. This statement is quantified with the help of Table 2 which reports, in terms of atom-centered coordinates, the intersection adapted coordinates for τ_x(cis,2.66,np), in the order ($\mathbf{x}$, $\mathbf{y}$, $\mathbf{z}^1$, $\mathbf{z}^2$, $\mathbf{z}^3$, $\mathbf{z}^4$). Note that $\mathbf{z}^3$ is the approximately

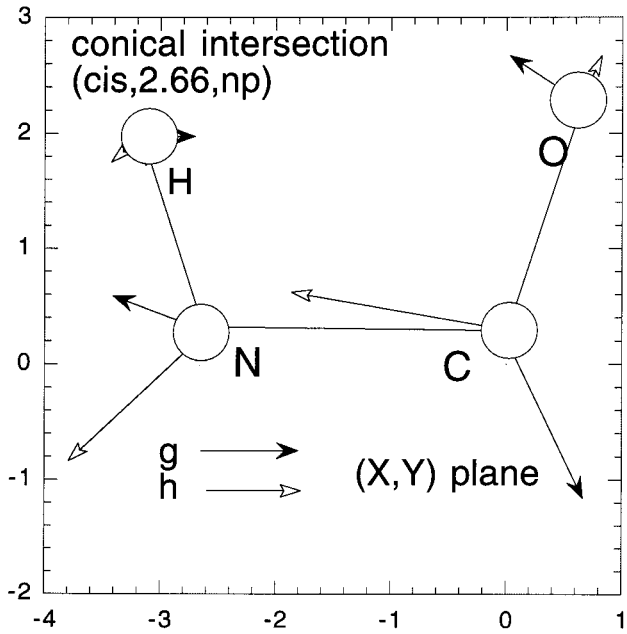

Figure 3. τ_x(cis, 2.66,np) open circles, scaled $\mathbf{g}^{IJ}$ filled arrows and scaled $\mathbf{h}^{IJ}$ open arrows.

TABLE 2: Intersection Adapted Coordinates for τ_x(cis, 2.66, np) in Terms of Atom Centered Coordinates (Atom A, Cartesian direction w)

Aw[a]	$\mathbf{g}^{IJ}$	$\mathbf{h}^{IJ}$	$\mathbf{z}^1$	$\mathbf{z}^2$	$\mathbf{z}^3$	$\mathbf{z}^4$
Hx	−0.011 600	−0.009 80	0.835 90	0.000 00	0.000 00	0.000 00
Hy	−0.002 000	0.074 30	−0.127 20	0.708 20	0.000 00	0.000 00
Hz	0.0115 00	0.001 00	0.013 80	−0.013 80	0.440 30	0.000 00
Nx	−0.519 500	0.332 60	−0.230 40	0.101 70	0.020 60	0.484 00
Ny	0.103 600	0.403 50	−0.090 20	−0.651 30	−0.017 10	0.126 00
Nz	−0.032 800	−0.015 90	0.003 40	0.010 50	−.602 80	0.006 40
Cx	0.530 700	0.357 10	−0.216 00	0.102 40	−.034 80	−.460 90
Cy	−0.513 50	−0.148 20	0.081 40	−0.097 80	0.040 60	−.577 00
Cz	0.0485 00	0.01740	−0.010 30	0.012 90	0.542 40	0.012 90
Ox	0.000 400	−0.679 90	−0.389 60	−0.204 10	0.014 20	−.023 10
Oy	0.411 90	−0.329 60	0.135 90	0.040 90	−.023 50	0.451 00
Oz	−0.027 300	−0.002 50	−0.007 00	−0.009 60	−.379 90	−.019 30

a'' mode. In this basis, $\mathbf{h}^{IJ}(\tau_x(\text{cis},2.65,\text{p})) = (-0.2134, -0.0781, -0.0505, 0.1164, \mathbf{-0.9623}$, and $-0.0582)$ and $\mathbf{g}^{IJ}$ $(\tau_x(\text{cis},2.65,\text{p}))$ $= (\mathbf{-0.9042}, \mathbf{-0.2790}, 0.0642, 0.0449, 0.2107$, and $0.1983)$. The bold face components demonstrate that $\mathbf{h}^{IJ}(\tau_x(\text{cis},2.65,\text{p}))$ is contained (largely) in the seam space of τ_x(cis,2.66,np). This confirms that this same symmetry point of conical intersection τ_x(cis, 2.66, np) and the symmetry-allowed point of conical intersection τ_x(cis, 2.65, p) reside on distinct branches of the $1^1\text{A} - 2^1\text{A}$ seam of conical intersection.

Note that criterion II is only approximately satisfied. This is attributed to the fact the τ_x are not sufficiently close (see Table 1) for the perturbative result to hold preicsely. This in turn is a consequence of the small value of h for points close to the confluence which sometimes makes locating such points difficult for our algorithm[24] which requires $\mathbf{g}^{IJ}$ and $\mathbf{h}^{IJ}$ to be non vanishing. Because this difficulty occurs principally for the symmetry-allowed seam it can be overcome by computing the symmetry-allowed crossing using wave functions with C_s symmetry imposed.[25] This approach will be used in a future publication, in which a discussion of the trans portion of the seam and a more complete mapping of this confluence will be presented.

IV. Summary and Conclusions

We report for the first time a confluence of two seams of conical intersection in a tetra-atomic molecule. The existence of the confluence is rationalized using perturbation theory. The confluence in question represents the intersection of an accidental symmetry-allowed conical intersection seam and an accidental same-symmetry conical intersection seam. The existence of intersecting seams of conical intersection significantly complicates the description of the overall intersection seam. It is, therefore, ironic to observe that the characterization of an accidental symmetry-allowed seam of conical intersection, here, the $^1\text{A}' - {}^1\text{A}''$ seam, is greatly facilitated by fact that it is symmetry-allowed. In this case, the energies can be determined from separate blocks of the Hamiltonian matrix, making an avoided intersection due to configuration interaction is impossible. However, as described in detail in section II, it is precisely this symmetry that makes a confluence with a same-symmetry seam is possible.

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