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Signatures of a Conical Intersection in Adiabatic Dissociation on the Ground Electronic State

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ABSTRACT: Conical intersections are known to cause nonadiabatic transitions, but their effects on adiabatic dynamics are often ignored. Using the overtone-induced dissociation of the hydroxymethyl radical as an example, we demonstrate that ground-state O−H bond rupture is significantly affected by a conical intersection with an electronically excited state along the dissociation path, despite the much lower energy of the dissociating state than that of the conical intersection. In addition to lifetime differences, the geometric phase leads to a different H_2CO rotational state distribution compared with that obtained using the standard single-state adiabatic model, which constitutes a signature of the conical intersection.

Conical intersections (CIs) invalidate the Born−Oppenheimer (BO) approximation as a consequence of their characteristic electronic degeneracy, shown in Figure 1. This degeneracy persists along an N-2-dimensional seam in the nuclear configuration space of a N-dimensional system.[1,2] Prevalent in polyatomic molecules,[3] it is well established that CIs play an essential role in many nonadiabatic processes,[4−7] including such basic biological processes as photosynthesis and vision.[8]

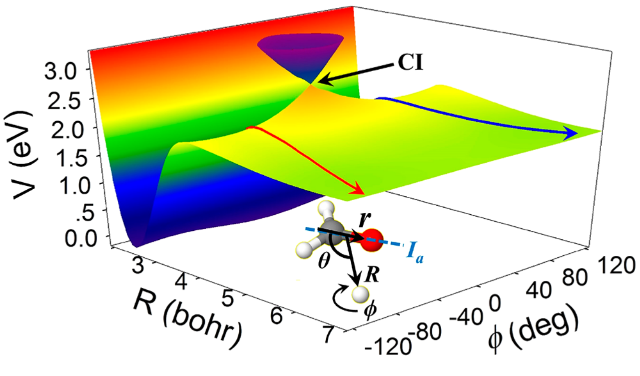

Figure 1. Adiabatic potential energy surfaces (PESs) of the two lowest electronic states of CH_2OH as a function of the R and ϕ coordinates with r = 1.436 Å, θ = 136.9°. The coordinates used in the four-dimensional (4D) model are shown in inset and defined below.

An extensively studied nonadiabatic process is internal conversion, where CIs serve as efficient funnels, facilely transferring population from an electronically excited state to a lower state.[9,10] While the role of CIs in internal conversion is intuitively clear, no such guidance is available for processes that begin and end on the same BO electronic state. The role of a CI in single-state dynamics is far from an arcane theoretical question because, for example, inference of barrier heights and curvatures from measured lifetimes is dependent on the validity of the standard adiabatic state description, which eschews the role of CIs. We have recently shown that owing to the participation of an energetically inaccessible CI, single-adiabatic-state tunneling dynamics in the S_1 state of phenol yield lifetimes that are in error by over a factor of 100,[11] precluding any inference of barrier characteristics. Thus, a signature of such a CI is vital to gain insights into a wide array of problems in contemporary chemistry.[12] Here, we examine CI-affected dissociation on a ground electronic state, and demonstrate and explain a signature property of the CI.

Nonadiabatic dynamics near a CI can be treated either in the adiabatic or diabatic representation.[13] Although these two representations are related by a unitary transformation, and thus are formally equivalent, the description of dynamics around a CI in the adiabatic representation reflects the geometric phase (GP), also known as Berry's phase.[14] This subtle but important difference arises from the fact that the adiabatic electronic wave function changes sign when transported around the CI.[15,16] The sign change renders the adiabatic electronic wave function double-valued, which needs be compensated for by a GP to ensure a single-valued total wave function. Hence, adiabatic nuclear dynamics near a CI can be significantly affected by the GP.[17−19]

One way to include the GP explicitly in the single-state adiabatic representation is the vector potential approach.[16,18,20−22] Such calculations can be numerically challenging because of singularities at the CIs. The significant overestimation by the adiabatic model of the tunneling lifetime

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in photodissociation of phenol[11] was shown to originate from the neglect of the GP, which was effectively corrected when the vector potential was included.[23−25] This is known as the Molecular Aharonov-Bohm effect,[26] where the upper adiabatic state is tacitly involved in the tunneling facilitated dissociation on the lower adiabatic state through the GP, even when the energy is well below that of the CI. Interestingly, the GP is implicitly included in the diabatic representation, because the diabatic electronic wave function is single-valued by construction. Indeed, most modern quantum treatments of nonadiabatic dynamics employ approximate diabatic representations.[13,27] However, diabatizations cannot be rigorously performed for polyatomic systems.[28,29] In addition, the computational expedience of the necessarily multistate diabatic representation sacrifices the appealing single-state picture provided by the BO representation.

It is desirable to identify measurable signatures of a CI and its associated GP. For bound-state Jahn−Teller systems, it is the well-known half-integer quantum numbers.[30,31] However, the signatures of CIs are less known in unimolecular dissociation on the lowest BO electronic state. To find such a signature, we consider the ground-state dissociation of the hydroxymethyl radical (CH_2OH). CH_2OH dissociation in both the ground and excited electronic states has been investigated extensively by Reisler.[32−38] In UV photodissociation, the excited radical fragments via one of several CIs.[39,40] Full-dimensional analytical PESs for low-lying electronic states have been constructed in a quasi-diabatic representation, using a high-level ab initio method.[41,42] Multistate reduced-dimension nonadiabatic quantum dynamics calculations on these PESs have successfully characterized the O−H fragmentation into the formaldehyde (H_2CO) + H channel via photoexcitation of the 3s Rydberg state.[43,44]

We focus here on dissociation of CH_2OH via overtone excitation, which accesses predissociative vibrational states on the ground electronic state above the $H_2CO(X)$ + H dissociation limit. Significantly, the product state distributions have been measured,[36,37] and theoretical simulations have been performed with quasi-classical trajectories (QCT) using the standard single-state adiabatic model.[45] Such overtone-induced dissociation differs from UV photodissociation in that the initial and final states are both on the ground Born-Oppenheimer state. Shown in Figure 1, there exists a CI between the ground and first excited states, flanked by two saddle points. Also present in the S_1 state of phenol,[11] this is a commonly encountered topography for CIs. Despite the existence of this CI, however, it is tempting to treat the overtone-induced dissociation adiabatically on the ground-state PES, as the minimum energy crossing of the CI (19054 cm^{-1} above the PES minimum) is higher in energy than many predissociative overtone states. Indeed, the QCT simulation noted above[45] using the prevailing theory of unimolecular reactions,[46,47] relied on this simplification. Thus, the question to be addressed here is whether the single-state adiabatic model is able to give a correct characterization of dissociation dynamics in the presence of the CI.

To this end, the ground-state dissociation dynamics of CH_2OH is treated in both adiabatic (no GP) and diabatic (GP implicitly included) representations. The former is based on the ground-state adiabatic PES, whereas the latter includes both the ground and first excited states and their coupling. Consequently, the difference between the two representations highlights the impact of the GP in the dissociation dynamics. Both models use as coordinates, the H−O (R) and C−O (r) bond stretches, the C−O−H bend (θ), and the H−C−O−H torsion (ϕ) (see Figure 1). The total rotational angular momentum of the system is assumed to be zero. With other coordinates fixed, these 4D models are sufficient to characterize the GP near the CI, as the active coordinates cover the branching space of the CI, which has its g and h vectors aligned roughly with the R and ϕ coordinates, as presented and discussed in the Supporting Information (SI). The C−O bond needs be included because of the large change of its length during dissociation. To ensure an accurate description of the PESs near the CI, additional ab initio points were calculated and used to generate a new fit of the diabatic PESs, as detailed in the SI. Importantly, the 4D model allows the determination of the $H_2CO(X)$ internal excitation, which can be measured.

The dynamics is followed by propagating Chebyshev wavepackets,[48] initiated as the ground vibrational state wave function multiplied by a model dipole moment (see SI). The Fourier transform of the autocorrelation function yields the energy spectrum corresponding to the overtone excitation. For narrow resonances, the low-storage filter diagonalization method[49] was used to extract lifetimes. Figure 2 compares the absorption spectra obtained from the adiabatic and diabatic models in the region of the third overtone excitation ($\nu_{OH} = 4$) for CH_2OH. It can be seen from the figure that the shapes of the spectra obtained from the two models are similar. The pronounced peaks correspond to predissociative resonances. The positions and lifetimes of five resonances are listed in Table 11. There are small energy differences (5−20 cm^{-1}) between the adiabatic and diabatic models. The lifetimes, which are state-specific, are close for some, but differ for others.

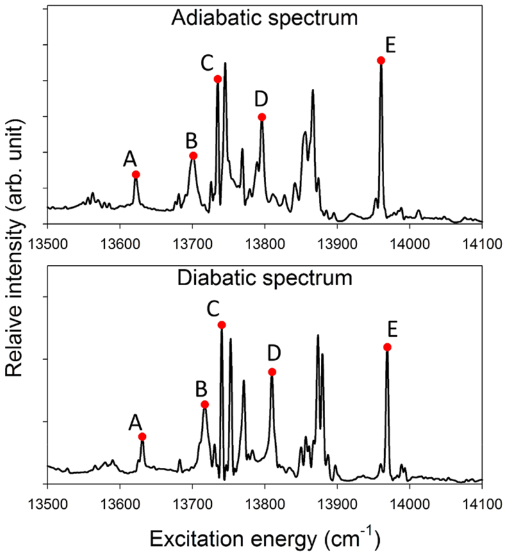

Figure 2. Overtone spectra of CH_2OH on its ground electronic state, obtained using the 4D adiabatic and diabatic models. Five predissociative resonances A−E are indicated by the red dots.

The difference in the lifetimes is a gauge of the influence of GP in dissociation. The relatively small (at most a factor of 2) difference seen here are in sharp contrast to phenol photodissociation, where the adiabatic lifetime is about 100 time shorter than its diabatic counterpart.[11] One might be tempted to conclude from the small differences between the adiabatic and diabatic lifetimes in the current system that the

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Table 1. Energies (ε in cm^{-1} related to the ground vibrational state) and Lifetimes (τ in ps) of the Predissociative Resonances A–E shown in Figure 2

	Adiabatic		Diabatic	
Peak	ε	τ	ε	τ
A	13622.1	1.55	13630.8	1.60
B	13701.4	0.73	13717.1	0.58
C	13735.1	8.49	13740.5	15.6
D	13795.9	0.94	13810.1	1.45
E	13960.5	2.65	13969.3	2.49

GP has a small influence on the dissociation dynamics. However, this is only partly true. In Figure 3, moduli and real parts of two resonance wave functions on the ground electronic state are displayed with the C–O–H angle and C–O distance fixed. It is clear that the wave functions from the two-state diabatic model, which implicitly includes the GP, possess a node at $\phi = 0$ outside the CI ($R > 3.55$ bohr), whereas this node is absent in the wave functions from the single-state adiabatic model where the GP is not included.

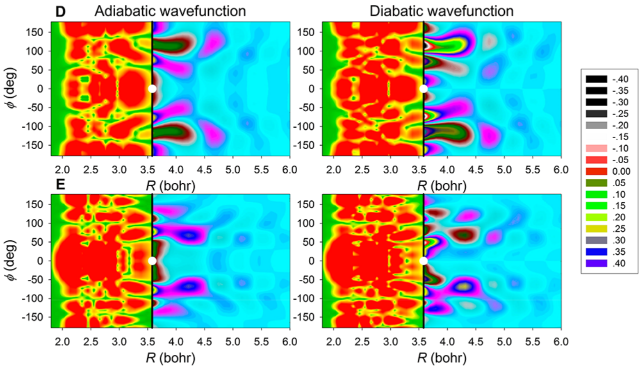

Figure 3. Moduli (left) and real parts (right) of cross sections of 4D wave functions on the ground-state PES as a function of (R, ϕ) for the resonances D and E, obtained from the single-state adiabatic and two-state diabatic models. The CI position is marked by a dot.

The well-known node of the adiabatic wave function near a CI is attributable to the GP.[16,50−54] As discussed by Althorpe,[55,56] it can be understood in the GP-corrected adiabatic picture as the result of destructive interference between two types of quantum "trajectories" passing around the CI on the opposite sides. Because these two "trajectories" possess opposite GPs due to their topologically different paths, they interfere destructively at $\phi = 0$ outside the CI, leading to a node in the wave function. In the case of phenol, a large difference in tunneling lifetimes was attributed to the strong destructive interference between two such types of tunneling "trajectories",[11,23,24] making the lifetime significantly longer than the counterparts obtained with a BO treatment. Interestingly, such strong interference was possible there because the topography of the adiabatic PES is such that the tunneling "trajectories" are attracted toward the planar geometry. Here, however, the PES topography is mostly repulsive along the ϕ coordinate near $\phi = 0$, so that the trajectories on the two sides of the CI, shown in Figure 1 by the two colored lines, are repelled away from $\phi = 0$, minimizing the interference.[25] This divergence is also seen in the wave functions (Figure 3). Consequently, the destructive interference, represented by the wave function node outside the CI, is still present, but has a small effect on the dissociation lifetimes.

Despite the relatively small impact of the GP on dissociation lifetimes, it is clear from Figure 3 that wave functions with and without the GP are fundamentally different. Most importantly, the symmetry of the asymptotic wave function in the ϕ coordinate depends on whether GP is included or not. The change of wave function symmetry in ϕ from inside to outside the CI, which leads to the node at $\phi = 0$, is a hallmark of the GP[15,50−54] and it is manifested in the product state distribution. Indeed, the $H_2CO(\nu_{CO} = 0)$ rotational state distribution from the single-state adiabatic model, as displayed in Figure 4, consists of only even-parity states because the GP is ignored. This is in sharp contrast with the two-state diabatic case where the GP is implicitly included and only odd-parity states are populated. This product distribution, which is a manifestation of the GP effect, should be detectable, thus providing a measurable signature of the GP effect near a CI in adiabatic dissociation. Unfortunately, the existing experimental data based on the H atom kinetic energy release[37] have insufficient resolution to detect it. However, the GP influence on product state distributions has been noted in phenol photodissociation,[57] where the h vector is along the C–C–O–H out-of-plane coordinate. There, only populations in odd quanta states are allowed for out-of-plane vibrational modes of the phenoxyl fragment. Experimental data seem consistent with this conclusion.[58,59]

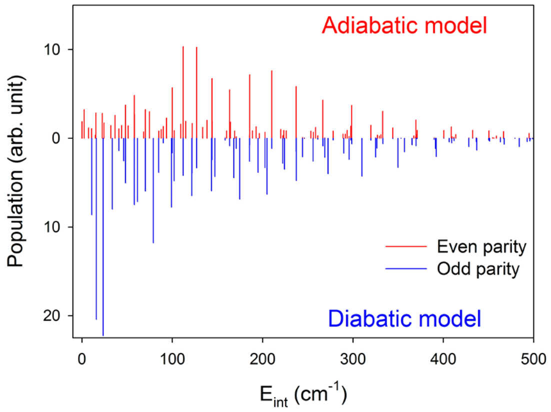

Figure 4. Rotational state distributions of $H_2CO(\nu_{CO} = 0)$ from the single-state adiabatic and two-state diabatic models for resonance A.

Summarizing, theoretical results presented here demonstrate unequivocally that in the presence of a CI, a single-state adiabatic treatment of dissociation processes is fundamentally flawed because of its neglect of the GP. The GP can significantly impact the lifetime and/or product state distributions. Consequently, a proper treatment should either use a multistate diabatic representation or adiabatic representation with explicit incorporation of the GP, even when the energy of the dissociating resonance is well below the CI. Furthermore, comparing the product rotational state distributions obtained in the standard single-state adiabatic formulation with the correct diabatic formulation shows the profound effect of the GP.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.7b11489.

Details of the model and calculations (PDF)

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Notes

The authors declare no competing financial interest.

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