Review Article

Exploring Multiple Potential Energy Surfaces: Photochemistry of Small Carbonyl Compounds

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In theoretical studies of chemical reactions involving multiple potential energy surfaces (PESs) such as photochemical reactions, seams of intersection among the PESs often complicate the analysis. In this paper, we review our recipe for exploring multiple PESs by using an automated reaction path search method which has previously been applied to single PESs. Although any such methods for single PESs can be employed in the recipe, the global reaction route mapping (GRRM) method was employed in this study. By combining GRRM with the proposed recipe, all critical regions, that is, transition states, conical intersections, intersection seams, and local minima, associated with multiple PESs, can be explored automatically. As illustrative examples, applications to photochemistry of formaldehyde and acetone are described. In these examples as well as in recent applications to other systems, the present approach led to discovery of many unexpected nonadiabatic pathways, by which some complicated experimental data have been explained very clearly.

1. Introduction

In order to theoretically unravel the entire photochemical reaction processes of a given system, one has to explore and characterize systematically several excited as well as the ground state potential energy surfaces (PESs). In the Franck-Condon (FC) approximation, a reaction starts from the FC point on an excited state PES. Then, the system undergoes either adiabatic or nonadiabatic pathways depending on a given excess energy and topographies on the PESs. In adiabatic paths, a bond reorganization occurs directly on the excited state PES through transition states (TSs). In nonadiabatic paths, on the other hand, the system makes nonadiabatic transition to a lower PES and then reacts on the lower PES. The system may cascade through several PESs via nonadiabatic transitions. Seams of intersection between two PESs often play a key role in various reactions [1–7]; near an intersection seam, nonadiabatic transitions

can take place efficiently. When the two states have the same spin and space symmetry, the intersection hyperspace consists of f-2 dimensions and is called "conical intersection (CI)," where f is the number of vibrational degrees of freedom. If the spin multiplicity and/or the space symmetry are different, the PESs cross simply in f-1 dimensional hyperspace. In this paper, both of these two types of intersections, that is, conical intersection and simple intersection seam, are denoted as "seam-of-crossing." In many kinetic studies, minimum energy structures on seam-of-crossing hyperspaces (MSXs) have been searched as critical points of nonadiabatic transitions. In short, to find all possible photochemical reaction pathways of a given system, systematic search for TSs and MSXs is required for all PESs below a given photon energy.

There have been considerable efforts on development of geometry optimization methods for MSXs [8–16] as well as for TSs [17–26]. A variety of geometry optimization

techniques, such as the gradient minimization [17, 18], the Berny optimization [19, 20], the eigenvector following [21], the geometry direct inversion in the iterative subspace [22], and the rational function optimization [23], have been a great help to locate the exact saddle point starting from a guessed TS structure. MSX optimization methods can be classified into three types: constrained optimization methods [8–10], the direct gradient (DG) method [11, 12], and penalty function (PF) methods [13, 14]. These methods were compared systematically, and the former two were shown to converge more quickly than a PF method [15]. On the other hand, PF methods have a significant advantage that nonadiabatic coupling derivative vector (CDV) calculations are not required in optimization of MSXs of the conical intersection type. Recently, CDV calculations can be avoided even in constrained optimization methods and in the DG method by using the branching plane updating method [16]. These methods have been successfully applied to many theoretical analyses of photochemical reactions.

In general, geometry optimization requires a good initial guess. However, guesses of MSX structures are sometimes very difficult, because their shapes are often highly deviated from those of stable molecular structures. A similar problem sometimes arises also in the search for TSs on a single PES. To avoid this problem, many automated TS (or minimum energy path) search methods have been developed [27–42]. Although most of these require guesses of a reaction mechanism such as key structures (product and intermediates) [27–34] or chemically relevant collective variables [35–37], some (relatively expensive) methods do not use any guess [38–42]. We also have developed two unique methods without needing any guess: the global reaction route mapping (GRRM) [43–45] method and the artificial force-induced reaction (AFIR) [46–48] method. GRRM can execute global mapping of reaction path networks of unimolecular isomerizations and dissociations on PESs of given atomic composition. AFIR can efficiently explore associative reaction paths among given reactants of multicomponent reactions. Although application of these automatic TS search methods to excited state PESs seems to be straightforward, it had not been successful probably because there are singular points in low-energy regions of excited state PESs due to conical intersections as discussed in Section 2.1. There has been no practical method for the automated MSX search either.

In this paper, we describe a recipe for exploring multiple PESs automatically. Two model functions, F^{AMF} and F^{SMF} [49, 50], are introduced for the TS search and the MSX search, respectively, in combination with the GRRM method. Although, in this study, it is applied to photochemical reactions, it can be applied to other nonadiabatic reactions such as ion-molecule reactions, organometallic reactions, and combustion reactions. Furthermore, the present recipe can adopt, instead of GRRM, any automated reaction path search method such as AFIR. In the present paper, we apply the proposed recipe with the GRRM method to photodissociation mechanisms of small carbonyl compounds such as formaldehyde H_2CO and acetone $(CH_3)_2CO$ [49, 51].

2. Theory

2.1. Avoiding Model Function (AMF) Approach. Figure 1(a) schematically illustrates a one-dimensional cut of two coupled adiabatic PESs. Along the curve for the upper PES, there is a local minimum in the left-hand side and a conical intersection in the right-hand side. In the conical intersection, the adiabatic PES is singular due to the coupling between two diabatic surfaces. To eliminate the singular point from the adiabatic PES, we use the following avoiding model function in automated search:

$$F^{AMF}(\mathbf{Q}) = \frac{1}{2}\left(E^{State\ 1}(\mathbf{Q}) + E^{State\ 2}(\mathbf{Q})\right)$$
$$+ \frac{1}{2}\sqrt{(E^{State\ 1}(\mathbf{Q}) - E^{State\ 2}(\mathbf{Q}))^2 + 4U^2},$$
$$U(\mathbf{Q}) = \frac{\alpha}{2}\exp\left[-\left(\frac{E^{State\ 1}(\mathbf{Q}) - E^{State\ 2}(\mathbf{Q})}{\alpha}\right)^2\right], \quad (1)$$

where $\mathbf{Q}$ is the atomic coordinates $\{Q_i\}$, $E^{State\ 1}(\mathbf{Q})$ is an adiabatic PES of the target (upper) state, $E^{State\ 2}(\mathbf{Q})$ is an adiabatic PES of the lower state, and α is a constant parameter. This F^{AMF} is very similar to the well-known equation for the diabatic/adiabatic transformation for two state systems, where $E^{State\ n}$ should be diabatic energies in the equation. In this study, adiabatic energies were substituted for $E^{State\ n}$. As seen in Figure 1(b), the model coupling function U in (1) changes the conical intersection region to an avoided crossing-like smooth curve. Thus, any automated search methods that require a smooth PES can be applied to F^{AMF}. TSs on F^{AMF} may be meaningless if the difference between F^{AMF} and $E^{State\ 1}$ is significant in TS regions, and therefore U was designed to have effects only in limited regions with a small energy gap. Hence, in TS regions F^{AMF} is often very similar to $E^{State\ 1}$. The accuracy (how well TSs on F^{AMF} reproduce TSs on $E^{State\ 1}$) depends on the value of α. To our experience, α should be about 1/10 of the vertical excitation energy of target reactions. In this study, we use $\alpha = 30$ kJ/mol throughout.

An example is shown in Figure 1(c) for the direct dissociation channel of H_2CO on the S_1 PES. Starting from S_1-TS, the backward IRC (intrinsic reaction coordinate) reaches S_1-MIN, while the forward IRC crosses S_0/S_1-MSX (conical intersection) in a partially dissociated region. Behind these (true) critical structures, local minima and a saddle point on F^{AMF} (with $\alpha = 30$ kJ/mol) are shown in black. As seen in Figure 1(c), the saddle point structure on F^{AMF} perfectly overlaps with S_1-TS (identical within convergence criteria of geometry optimization: maximum absolute gradient $g_{MAX} = 6.0 \times 10^{-5}$ hartree Å^{-1}, root mean square gradient $g_{RMS} = 4.0 \times 10^{-5}$ hartree Å^{-1}, maximum absolute displacement $d_{MAX} = 3.0 \times 10^{-4}$ Å, root mean square displacement $d_{RMS} = 2.0 \times 10^{-4}$ Å). S_1-MIN is also reproduced perfectly by the minimum on F^{AMF}. Moreover, on F^{AMF}, S_0/S_1-MSX turned into a local minimum shown in black behind S_0/S_1-MSX. In other words, the conical intersection does not exist on F^{AMF}, which enables exploring the smooth F^{AMF} with an automated reaction path search method.
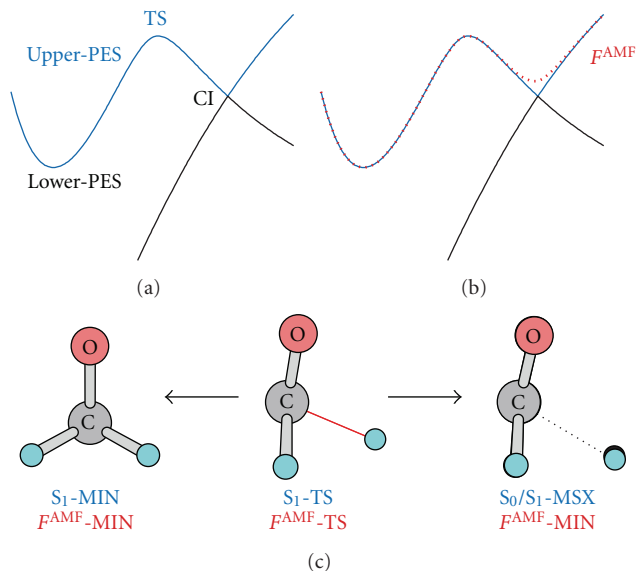
FIGURE 1: (a) A schematic one-dimensional curve of two coupled adiabatic PESs, (b) an example of F^{AMF} for the PESs in (a), and (c) comparisons between stationary points on F^{AMF} (with $\alpha = 30$ kJ/mol) and those on the S_1-PES of H_2CO (see Section 2.4 for the ab initio calculation level). Each structure shown in (c) corresponds to S_1-MIN, S_1-TS, and S_0/S_1-MSX (conical intersection), respectively, and stationary structures on F^{AMF} are overlapped in black behind them. At S_1-MIN and S_1-TS, the stationary structures on F^{AMF} are identical to them within the convergence criteria (see text) of geometry optimization and cannot be seen. F^{AMF}-MIN can barely be seen behind S_0/S_1-MSX.

In short, TSs on an excited state (adiabatic) PES $E^{State\ 1}$ can be explored in two steps: a search for many TS-like structures as first-order saddles on F^{AMF} by an automated search method, optimization of true TSs on the PES $E^{State\ 1}$ using the TS-like structures as initial guesses. It should be noted that all TSs shown below are fully optimized first-order saddle points (true TSs) on adiabatic PESs.

2.2. Seam Model Function (SMF) Approach. In the automated search for MSXs, the following model function F^{SMF} is considered [49, 50]:

$$F^{SMF}(\mathbf{Q}) = \frac{1}{2}\left(E^{State\ 1}(\mathbf{Q}) + E^{State\ 2}(\mathbf{Q})\right)$$
$$+ \frac{\left(E^{State\ 1}(\mathbf{Q}) - E^{State\ 2}(\mathbf{Q})\right)^2}{\beta}, \qquad (2)$$

where $\mathbf{Q}$ is the atomic coordinates $\{Q_i\}$, $E^{State\ 1}(\mathbf{Q})$ and $E^{State\ 2}(\mathbf{Q})$ are PESs of two target states, and β is a constant parameter. Minimization of F^{SMF} gives a geometry in which both the mean energy of the two states (the first term) and the energy gap between the two states (the second term) are small. Hence, minima on F^{SMF} can be good guesses of MSXs. Equation (2), which is also called penalty function (PF), or more complicated PFs have been employed in MSX geometry optimization [13, 14]. As discussed above, PF methods have a drawback concerned with convergence in MSX optimization

[15]. However, in automated searches, use of the PF has a significant advantage that the PF is a single smooth function, which permits the application of automated search methods developed for single PESs without any modification. Hence, we proposed the SMF approach which consists of two steps: (a) a search for many MSX-like structures as local minima on the PF using an automated search method and (b) determination of (true) MSX structures by using one of MSX optimization methods and MSX-like structures obtained in (a) as initial guesses.

Although smaller β gives better (more accurate) candidates, minimizations of F^{SMF} with smaller β need more optimization steps since at $\beta = 0$ the function becomes singular. This is the cause of the slow convergence of a PF method observed in the systematic comparative study. To avoid this, use of relatively large β (typically $\beta \sim 30$–50 kJ/mol) is recommended since the purpose of the first step (a) is to systematically collect many MSX-like structures as quick as possible. In this study, we use $\beta = 30$ kJ/mol throughout. It should be noted that all MSXs shown below are fully optimized true MSXs (the energy gap between two target states is smaller than 0.1 kJ/mol in all MSXs).

2.3. Global Reaction Route Mapping (GRRM) Method. In the GRRM method [43–45], global mapping of reaction path networks is executed by following the path network itself. To make such a search, one has to follow the paths in both uphill (minimum to saddle) and downhill (saddle to minimum) directions. The latter can be accomplished by following the IRC [52] using one of advanced steepest decent path methods [53–57]. The former, that is, uphill walk, had been difficult before 2004 until we proposed the anharmonic downward distortion following (ADDF) approach.

Many typical potential curves show a common feature that potential energy always become lower than the harmonic potential defined at the bottom of the curves in directions leading to TSs. Thus, reaction channels can be found by following ADD maxima starting from a local minimum on a PES. In many previous applications, the GRRM method based on the ADDF approach has found many unknown as well as nearly all known reaction channels automatically. The ADD maxima can be detected in multidimension by using the scaled hypersphere search (SHS) technique. Details of the SHS technique can be found in our previous papers [43–45].

Following all ADDs starting from all obtained local minima will provide an entire global map on PESs. Such a treatment called full-ADDF, denoted GRRM(f-ADDF), is very expensive, and its application is limited to small systems. An approach following only large ADDs, large-ADDF denoted GRRM(l-ADDF), is effective to survey low-energy regions of PESs in large systems [58]. Another useful option for speedup is double-ended ADDF, denoted GRRM(d-ADDF), which confines the search area between given reactant and product geometries [33, 34].

2.4. Computational Methods Used in Applications. In this section, we summarize quantum chemical methods used in the applications in the following sections. For details, see original articles [49, 51].

In an application to H_2CO, GRRM(f-ADDF) was applied to F^{SMF} at the 3SA-CAS(4e,3o)-SCF/6-31G and 3SA-CAS(2e,3o)-SCF/6-31G levels, where SA stands for state-average and the averaged three states are S_0, S_1, and T_1. All obtained MSX-like structures were fully optimized at the 2S-CAS(12e,10o)-PT2/aug-cc-pVDZ level for the singlet states and at the SS-CAS(12e,10o)-PT2/aug-cc-pVDZ level for the triplet state, where 2S and SS stand for two-state averaged and single-state, respectively. In the state averaging, equal weights were used. All (known) TSs and local minima on these PESs were optimized at the same (CASPT2) levels.

In an application to $(CH_3)_2CO$, GRRM(d-ADDF) was applied to F^{SMF} and F^{AMF} at the 2SA-CAS(8e,7o)-SCF/6-31G and SS-CAS(8e,7o)-SCF/6-31G levels for the S_0, S_1, and T_1 states, respectively, where SS here stands for state-specific. In addition to $(CH_3)_2CO$, three isomers, $CH_2=C(OH)-CH_3$ (enol), $^\bullet CH_2-CH(O^\bullet)-CH_3$ (biradical), and $CH_3-CO-CH_3$ (carbene), and a partially dissociated geometry $CH_3CO\cdots CH_3$ were considered as the end points for d-ADDF. All obtained MSX-like structures and TS-like structures were fully optimized at the 2S-CAS(8e,7o)-PT2/6-31+G* level for the singlet states and at the SS-CAS(8e,7o)-PT2/6-31+G* level for the triplet state. Local minima were optimized also at the same (CASPT2) levels.

Potential energies and gradients required for the searches as well as optimization were computed by the Molpro2006 program [59]. Using these quantities, all geometrical displacements were treated by the GRRM11 program [60].

3. Photodissociation of Formaldehyde

It was suggested experimentally that the photodissociation of H_2CO at low-photon energies occurs on the S_0 PES after an internal conversion (IC) from the S_1 PES [61–65]. Hence, dynamics as well as stationary points on the ground state S_0 PES have been studied extensively by theoretical calculations [39, 40, 43–45, 66–89]. The focuses in early studies had been on the following two channels:

$$H_2CO \longrightarrow CO + H_2, \tag{3}$$

$$H_2CO \longrightarrow HCO + H, \tag{4}$$
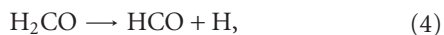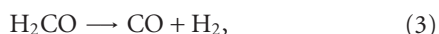
The TS for the channel (3), which is often called "tight-TS," was already determined in 1974 by ab initio calculations [67]. The radical dissociation (4) can occur both from the S_0 PES and from the T_1 PES, and hence the T_1 PES has also been studied [90, 91]. Knowledge of the higher singlet states was rather scarce until very recently [92, 93]. A new channel for the molecular products was experimentally proposed in 1993 [94]; the channel is often represented as

$$H_2CO \longrightarrow HCO \cdots H \longrightarrow CO + H_2, \tag{5}$$
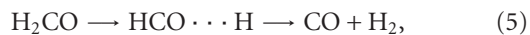
where one of H atoms, once partially dissociated, roams around the HCO fragment and finally abstracts the other H atom to generate $CO + H_2$. This speculation was confirmed in 2004 by combined experimental and theoretical studies [95]. Since its discovery, this channel named "roaming" has

been a hot topic as a new type of reaction mechanism [96–98], and it has been found in many reactions having implications to atmospheric chemistry [99–108] and combustion chemistry [88, 109, 110].

The IC was postulated to occur in the potential well of H_2CO in many previous studies. However, recently, several MSXs were found outside the potential well of H_2CO: two S_0/T_1-MSXs were located in the potential well of hydroxycarbene HCOH [111, 112], a S_0/S_1-MSX was located in a partially dissociated $H \cdots HCO$ region [113]. In 2009, we explored multiple PESs for the S_0, S_1, and T_1 states by the SMF-GRRM approach [49]. The potential energy profile we discovered is presented in Figure 2, where the high-energy regions for $H_2O \cdots C$ and $H_2C \cdots O$ are not shown. The two S_0/T_1-MSXs of HCOH [111, 112] are denoted as S_0/T_1-MSX2 and S_0/T_1-MSX3, and the partially dissociated S_0/S_1-MSX [113] is shown as S_0/S_1-MSX1. As seen in this figure, to isomerize on the T_1 PES or to partially dissociate on the S_1 PES, the system has to overcome a significant barrier. At low-photon energies ($<32\,000\,cm^{-1} = 383\,kJ\,mol^{-1}$), these barriers are not accessible. Hence, these known MSXs are not likely involved in the low-energy photodissociation process.

In addition to known MSXs, some new MSX structures were discovered in the automated search. One of those, S_0/T_1-MSX1, was discovered in the potential well of H_2CO. Adopting this new S_0/T_1-MSX1 and known excited state TSs [111, 114], we proposed the entire mechanism for the low-energy photolysis as follows. After the photoexcitation the system oscillates around the S_1-MIN for a long time since there is no S_0/S_1-MSX in the potential well and the lowest S_1/T_1-MSX1 is higher than the photon energies. The S_1/T_1 intersystem crossing (ISC) may be able to take place by trickling down from S_1 to T_1 at all the geometries, while the molecule in the S_1 state spends a long time oscillating around S_1-MIN, because PESs for the S_1 and T_1 states are very close and nearly parallel to each other in energy at any place in the basin of S_1-MIN. Although the probability at each geometry may be small because the spin-orbital coupling between the two states belonging to the same electronic configuration is small, the integrated probability over a long time could be substantial. Once the system comes down to T_1 from the S_1-MIN basin region, the T_1/S_0 ISC via the newly found S_0/T_1-MSX1 ($390\,kJ\,mol^{-1}$) can take place in this H_2CO basin. This mechanism based on the CASPT2 energetics is consistent with the result obtained by the MRCISD(Q)/AV5Z calculations, where relative energy values of the three important barriers, that is, the S_1 (C–H bond scission) barrier, the T_1 barrier, and S_0/T_1-MSX1, are 456.4, 413.1 and 397.7 kJ/mol, respectively, at the MRCISD(Q)/AV5Z level [114]. After the transition to S_0, the dynamics on the S_0 PES should start in the H_2CO basin and propagate via the tight-TS or the roaming pathway to give the $CO + H_2$ product.

After the proposal of this mechanism, direct CASSCF dynamics studies have been conducted for the molecular dissociation at medium excitation energies [115, 116]. By these simulations, molecular dissociations involving an ISC or a direct IC in the partially dissociated $H \cdots HCO$ region were proposed. These paths undergo a C–H bond dissociation
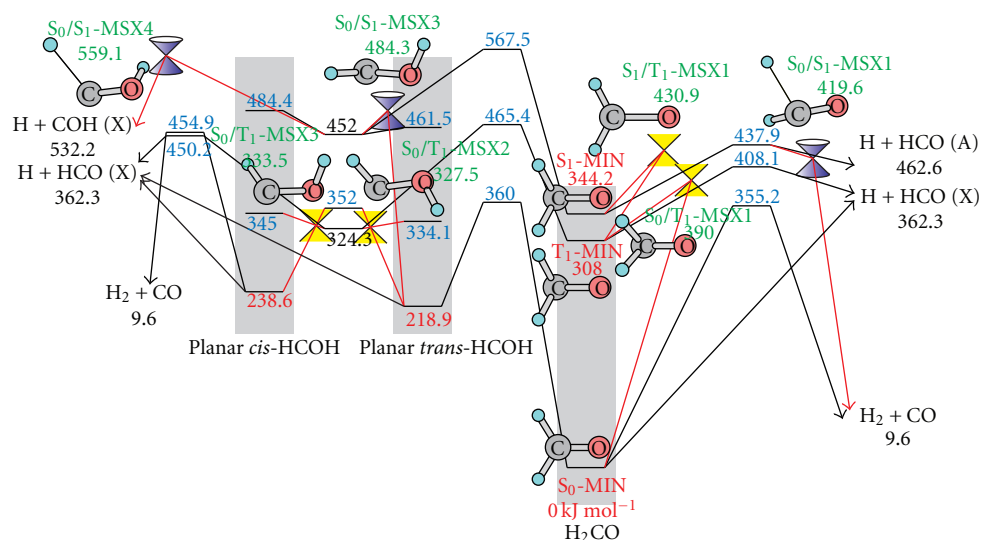
FIGURE 2: A CASPT2 potential energy profile (in kJ/mol) for the three low lying S_0, S_1, and T_1 states of H_2CO [49]. Reprinted with permission from [49]. Copyright 2009 American Chemical Society.

on either the T_1 or S_1 PESs. Obviously, the S_1 dissociation needs sufficient (medium) photon energies to overcome the S_1 barrier. The other path involving the partial dissociation on the T_1 PES may happen via tunneling or zero-point-energy effect even at the low photon energies. However, this (molecular dissociation involving the T_1 dissociation) was shown to be a very minor process in recent three-state trajectory surface hopping (3S-TSH) simulations including the S_0, S_1, and T_1 states [117]. In the 3S-TSH simulations, highly accurate (analytically fitted) PESs were employed and the hopping was treated by Tully's fewest switches algorithm. The 3S-TSH simulations demonstrated that the above decay mechanism involving the S_1-T_1 trickling down mechanism followed by the T_1-S_0 ISC through S_0/T_1-MSX1 in the potential well of H_2CO is the major process before the molecular dissociation. Furthermore, they discovered a new unexpected (but minor) dynamics in which the system once decays down to the S_0 PES and then isomerize to HCOH on the S_0 PES before the dissociation. Surprisingly, in such trajectories, the system hops up to the T_1 PES and then hops down to the S_0 PES through S_0/T_1-MSX1 or S_0/T_1-MSX2. This is energetically certainly allowed in Figure 2.

4. Photodissociation of Acetone

Another example is an application to $(CH_3)_2CO$ [51]. Photolysis of acetone is one of the most extensively studied photochemical reactions [118]. The CC bond dissociation, called "Norrish type I reaction" $(CH_3)_2CO \rightarrow CH_3CO + CH_3$, has been the main focus of many theoretical and experimental studies [119–133]. Roaming was also suggested experimentally [102], which was proposed to proceed on the S_0 PES as $(CH_3)_2CO \rightarrow CH_3CO \cdots CH_3 \rightarrow CO + CH_3$–$CH_3$.

In early experimental studies [119–121], it was proposed that the Norrish type I dissociation occurs on the T_1 PES

(the T_1 path) after an ISC from the S_1 PES, as long as the photon energy exceeds the barrier of the CC bond breaking on the T_1 PES. A theoretical calculation at the CASSCF level indicated that the ISC happens around a S_1/T_1-MSX structure located below the T_1 barrier, and the T_1 path was suggested to be the most preferable channel (at least in terms of potential energy) [122]. However, in later combined femtosecond laser experimental and theoretical studies [123–125], it was suggested that the dissociation occurs through the S_1 barrier (the S_1 path) before the ISC takes place when photon energies are larger than the S_1 barrier. The S_1 path was then confirmed by another femtosecond laser study at 195 nm (613 kJ/mol) [126–128]. Relevant stationary structures for the S_1 path were examined by CASPT2 and MRCISD(Q) calculations [132]. We revisited [51] the PESs of $(CH_3)_2CO$ for two purposes: to find nonadiabatic paths to the S_0 PES systematically for the roaming channel and to explain the conflict between the fast S_1/T_1 ISC proposed by CASSCF calculations and the experimentally observed S_1 path which overcomes the S_1 barrier much higher than the CASSCF S_1/T_1-MSX.

Figure 3 presents a potential energy profile for the three low lying S_0, S_1, and T_1 states. For isomerizations on the S_1 and T_1 PESs, only the lowest channels for the $(CH_3)_2CO \leftrightarrow CH_2=C(OH)$–$CH_3$ reaction (S_1-TS2 and T_1-TS2) are shown in the profile. As seen in this figure, these excited state isomerizations have higher barriers and must be minor channels compared to the CC bond dissociations (S_1-TS1 and T_1-TS1). We should note that the S_1/T_1-MSX is much higher in energy than T_1-TS1 on the CASPT2 PESs in contrast to the case of the CASSCF calculations reported previously. Hence, if photon energy is higher than the S_1 barrier (S_1-TS1), the most favorable path is the direct dissociation. This explains the recent femtosecond laser experimental observation very well. Below the S_1 barrier, there is no exit channel from the S_1 PES. Hence and also because of very small spin-orbit
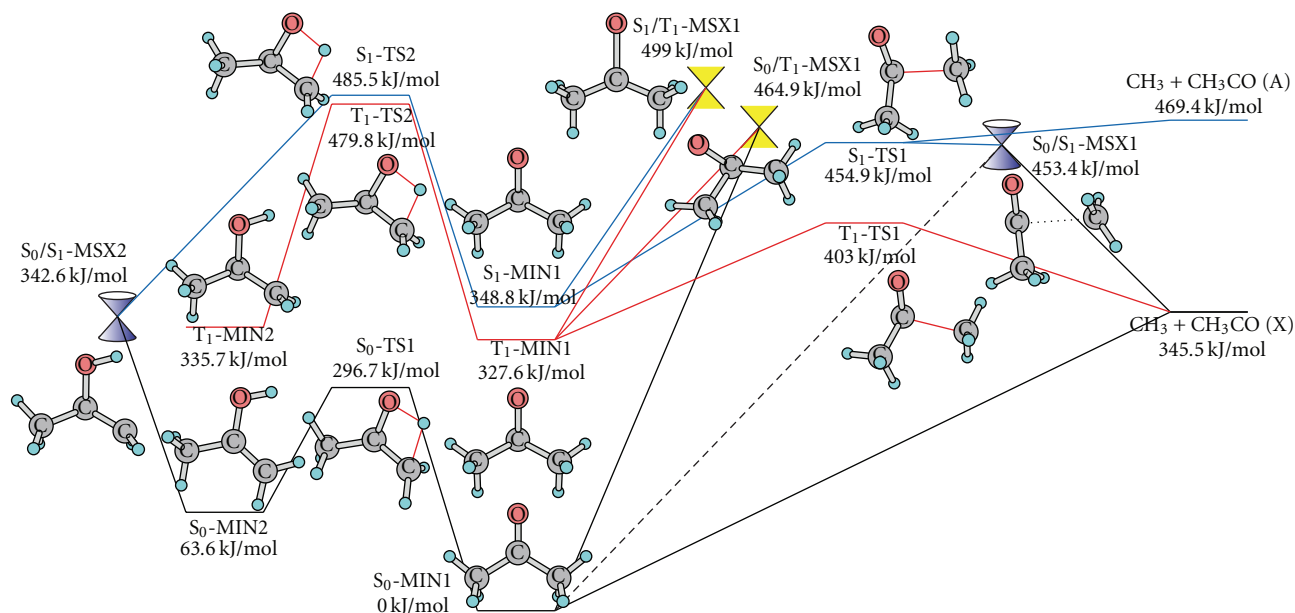
Figure 3: A CASPT2 potential profile for the three low lying states (S_0, S_1, and T_1) of $(CH_3)_2CO$ [51]. Reprinted with permission from [51]. Copyright 2010 American Chemical Society.

coupling between the S_1 and T_1 states, we proposed that the ISC occurs very slowly by trickling down from S_1 to T_1 while the molecule in the S_1 state spends a long time oscillating around S_1-MIN1. This may be able to happen because PESs for the S_1 and T_1 states are very close and nearly parallel to each other in energy at any place in the basin of S_1-MIN1, similarly to the case of H_2CO. There are some experimental evidences showing that the S_1/T_1 ISC is very slow [134]; recent time-resolved mass spectrometry and photoelectron spectroscopy experiments and direct dynamics simulations suggested that the system decays from the FC region to the S_1 minimum within 30 femtoseconds and then stays on the S_1 PES more than 100 picoseconds at 253–288 nm (473–415 kJ/mol) excitations [135, 136]. After coming down to the T_1 PES, the system can overcome the T_1 barrier to undergo the Norrish type I reaction.

In Figure 3, several decay paths can be found from the S_1 PES to the S_0 PES. Unlike H_2CO, S_0/T_1-MSX1 in the potential well of $(CH_3)_2CO$ is much higher in energy than T_1-TS1. The lowest path to the S_0 PES undergoes a dissociation on the S_1 PES through S_1-TS1 followed by a nonadiabatic transition in the nearly dissociated geometry through S_0/S_1-MSX1 and a recombination on the S_0 PES. The roaming dynamics was observed at 230 nm (520 kJ/mol) [102], at which the direct CC bond dissociation on the S_1 PES is the dominant path of the Norrish type I reaction. Hence, this is the most likely path to produce the ground state $(CH_3)_2CO$. At this photon energy, the excited state isomerization to the enol species followed by an IC through S_0/S_1-MSX2 and an enol-keto isomerization on the S_0 PES may be a minor channel to the ground state $(CH_3)_2CO$ before the roaming dynamics may take place.

5. S_0/T_1 Intersection Space

One can find candidates of saddle points on seam-of-crossing hyperspaces (SPSXs) as saddles on F^{SMF}. Minimum energy paths on seam-of-crossing hyperspaces (MEPSXs) starting from SPSXs were suggested to be useful for understanding dynamical trajectories crossing a high-energy region of a seam-of-crossing hyperspace [12]. In this section, SPSXs and MEPSXs for the S_0/T_1 intersection spaces of H_2CO and $(CH_3)_2CO$ are discussed because of their significance in the generation of the S_0 species. The optimization method for SPSXs from SMF (or guessed) structures and an algorithm to calculate an MEPSX from a SPSX are described in our previous paper [16].

Figure 4(a) shows a MEPSX for the S_0/T_1 intersection space of H_2CO at the CASPT2 level. The MEPSX was calculated from two SPSXs. Along the MEPSX, all points have the S_0/T_1 energy gap less than 1.0 kJ/mol. As seen in this figure, the S_0/T_1 intersection space was found to be connected from the HCOH area through the S_0/T_1-MSX1 geometry to the partially dissociated region. It follows that the S_0/T_1 ISC may take place not only at S_0/T_1-MSX1 but also with variety of geometries in this very wide intersection space.

Integration of an MEPSX with CASPT2 is expensive, and we also tested and used the UB3LYP method using Gaussian09 program [137]. At first, the MEPSX for H_2CO by the UB3LYP method is shown in Figure 4(b). For H_2CO the MEPSX by UB3LYP is similar to the one by the CASPT2 method. Therefore, we adopted the UB3LYP method for $(CH_3)_2CO$. Figure 5 shows two MEPSXs (a) for $H_2C=C(OH)CH_3 \leftrightarrow (CH_3)_2CO \leftrightarrow CH_3CO + CH_3$ and (b) for $CH_3–CO–CH_3 \leftrightarrow (CH_3)_2CO \leftrightarrow CH_3CO + CH_3$. Another MEPSX from an MSX of the $^\bullet CH_2–CH(O^\bullet)–CH_3$ form (not shown) is directly connected to the partially dissociated

(a)

(b)
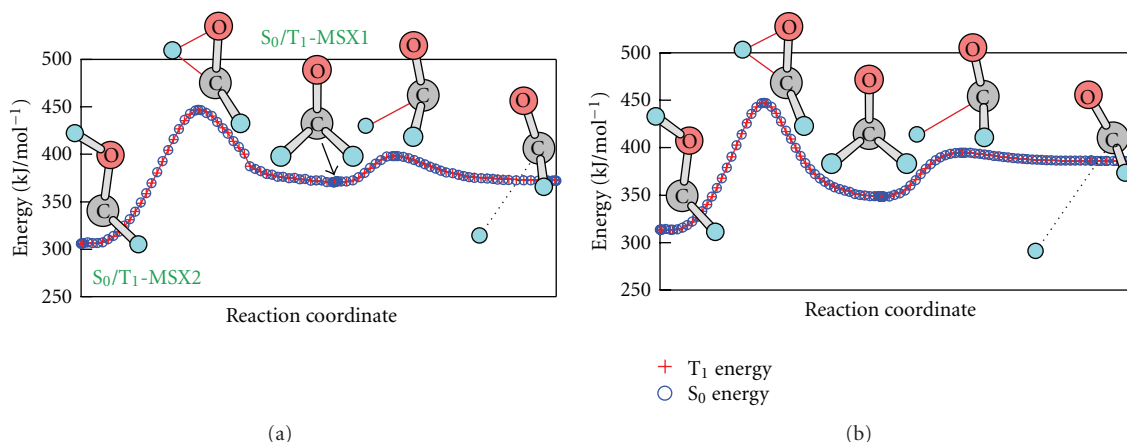
FIGURE 4: (a) A S_0/T_1-MEPSX curve for HCOH $\leftrightarrow$ H$_2$CO $\leftrightarrow$ HCO + H at the CASPT2 level (see Section 2.4 for details of the CASPT2 calculations) and (b) a S_0/T_1-MEPSX curve for the same reaction at the UB3LYP/aug-cc-pVDZ level.

CH$_3$CO $\cdots$ CH$_3$ region through only one SPSX structure, that is, it does not enter the potential well of (CH$_3$)$_2$CO. In contrast to Figure 4, these intersection spaces lie in a very high-energy region in the potential well of (CH$_3$)$_2$CO. Only outside the potential well, the intersection space comes down to a low-energy region. Thus, the S_0/T_1 ISC is expected to be much slower in (CH$_3$)$_2$CO than the case of H$_2$CO, although (CH$_3$)$_2$CO also has a very wide S_0/T_1 intersection space.

6. A Merit of Automated Search

The most significant advantage of the present approach is that unexpected pathways can be discovered. Geometry optimization has been a very powerful mean to locate exact MSXs and TSs starting from guessed geometries. However, a guess structure leads only to a TS or a MSX anticipated from it. On excited state PESs, molecules frequently take unexpected geometries that are very different from those of stable ground state molecules. Hence, the advantage of the present method without guess is very helpful in analyses of photochemical reactions.

We already reported some unexpected paths discovered by the present recipe. The first is the S_0/T_1 ISC path for H$_2$CO as discussed above [49]. The second is an H-atom roundtrip path discovered in photolysis of methyl-ethyl-ketone CH$_3$C(O)C$_2$H$_5$ [138]. In this path, on the S_1 PES, an H atom in the ethylgroup at first transfers to the O atom to undergo an S_0/S_1 IC in a conical intersection of a diradical isomer, and then the H atom comes back to the original position on the S_0 PES, and finally the molecule dissociates into CH$_3$CO + C$_2$H$_5$ or C$_2$H$_5$CO + CH$_3$ on the S_0 PES. This path explained an experimental photodissociation quantum yields measurements very well. The third is the discovery for the first time of the excited state roaming pathway, which we found in photolysis of NO$_3$ [107, 108]. Here, one of the O atoms in NO$_3$ partially dissociates on the first excited doublet (D$_1$) PES and then roams around the NO$_2$ fragment before producing O$_2$ + NO on either the D$_1$ PES or the ground state D$_0$ PES. This mechanism

also explained very well recent experimental results giving two channels, one with hot O$_2$ and the other with cold O$_2$ [105, 106]. Unexpected nonadiabatic ignition paths of unsaturated hydrocarbons were also discovered by the SMF-AFIR approach very recently [50].

7. Conclusion and Perspective

We reviewed our recipe to explore multiple PESs systematically by using an automated reaction path search method which has been used for the ground state (smooth) PESs [49, 50]. In this paper, it was applied together with the GRRM method [43–45] to small carbonyl compounds to study their photodissociation mechanisms. In an application to H$_2$CO [49], we discovered a new nonadiabatic (S_0/T_1 ISC) path to reproduce the ground state species in the potential well of H$_2$CO. This path was recently confirmed by extensive 3S-TSH simulations using very accurate PESs [117]. For (CH$_3$)$_2$CO [51], many possible nonadiabatic decay paths from the S_1 PES were systematically located, and new insight into the slow S_1/T_1 ISC and new nonadiabatic paths to the ground state PES were obtained.

Three or more states may couple simultaneously in some reactions. An extension of the present approaches is straightforward since both (1) and (2) are similar to the equation for the diabatic/adiabatic transformation, although we have not yet made systematic tests for such cases.

Dynamic effects may play a significant role in many reactions. Although direct dynamics is very useful in simulations with moderate accuracies [139], it is still too expensive to find all the reaction events of a given system including slow events. There are many powerful approaches applied to ground state PESs to accelerate a dynamics for known mechanisms [140–142]. A prior mechanism search by the present approach followed by such accelerated dynamics may be a solution in the future for theoretical solving complicated reaction mechanisms. The present method can also be connected to the analytical PES fitting approach [143–146] which enabled the recent extensive 3S-TSH simulations of
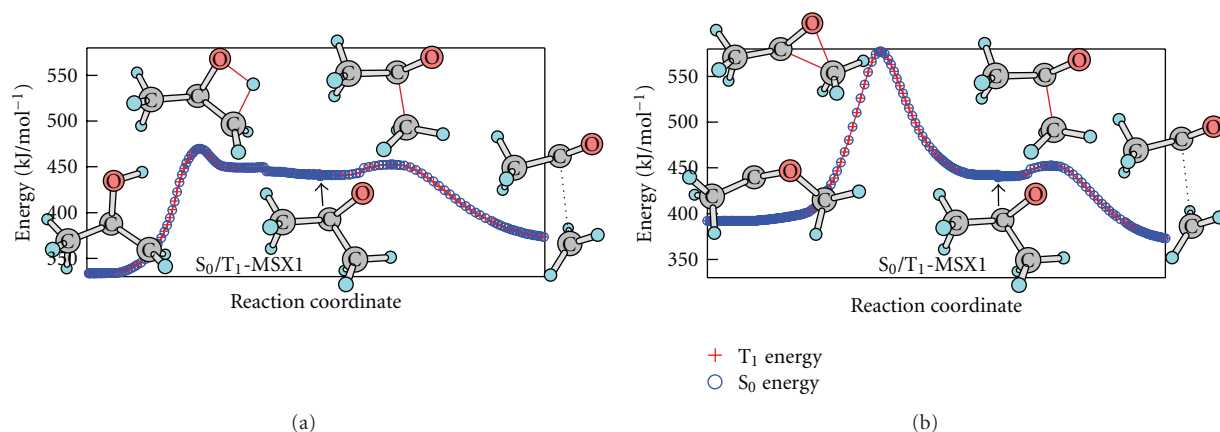
(a)

+ T$_1$ energy
○ S$_0$ energy

(b)

FIGURE 5: (a) A S$_0$/T$_1$-MEPSX curve for H$_2$C=C(OH)CH$_3$ ↔ (CH$_3$)$_2$CO ↔ CH$_3$CO + CH$_3$ and (b) a S$_0$/T$_1$-MEPSX curve for CH$_3$–CO–CH$_3$ ↔ (CH$_3$)$_2$CO ↔ CH$_3$CO + CH$_3$, at the UB3LYP/6-31+G* level.

H$_2$CO [117]. This approach permits the execution of highly accurate simulations, although applications are limited to small systems including less than 20 atoms. In constructing an analytical PES, prior knowledge about the mechanisms obtained by the present approach will be very useful for effective sampling of the PES data with the least number of ab initio calculations, avoiding exhaustive sampling on a perfect grid covering all configurations. One technical but significant issue in this approach is how to represent the square root topology of conical intersections, and several approaches have been proposed [147–150].

Our particular interest is to apply the present approach to multiple PESs described by combined quantum mechanical and molecular mechanical (QM/MM) calculations [151–154]. We have already reported automated reaction path search on the ground state PES of the QM/MM-ONIOM method [155] by combined microiteration [156, 157] and GRRM methods [158], where use of AFIR instead of GRRM has already been possible. This development is expected to greatly expand the applicability of the present approach to large systems.

Acknowledgements

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