From Roaming Atoms to Hopping Surfaces: Mapping Out Global Reaction Routes in Photochemistry

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INTRODUCTION

The photodissociation of small molecules plays important roles in atmospheric processes on the Earth’s surface, in the atmospheres of other planets, and in interstellar media. The accurate modeling of these processes is of great significance and requires kinetic data of all possible elementary reactions. Recently, quantum-chemical calculations combined with kinetic theories have become a powerful means for the prediction of atmospheric reaction rate constants that occur on the ground electronic state potential energy surface (PES). However, making similar predictions for photochemical reactions that involve excited electronic state PESs is not that simple for two reasons. One is the accuracy and efficiency of quantum-chemical calculations on excited electronic states. The other is that it is still difficult to find all of the feasible reaction pathways for high-energy molecules that involve excited electronic states as well as the ground state by a conventional geometry optimization approach. This Perspective presents our approaches to a resolution of the latter problem.

Another motivation for studies of the photodissociation of small molecules is to obtain a thorough understanding of the fundamental issues of these chemical reactions. The photodissociation of small molecules is relatively simple and is ideally suited for this purpose. In particular, the photodissociation dynamics of small molecules has been studied in great detail. One of the hottest topics in reaction dynamics over the last 10 years is “roaming”. This refers to a pathway to molecular products in a unimolecular reaction with a very different configuration space that describes the dissociation to radical products and a subsequent “self-reaction” of the radicals to form molecular products. This unusual pathway was suggested as the most likely of two possible mechanisms to explain a feature in the CO rotational distribution during the photodissociation of H2CO.6 A roaming pathway was found (and named) definitively in 2004 in joint theoretical/experimental work. Quasiclassical trajectory calculations in ref 6 showed that this unusual pathway is the one that leads to the shoulder feature in the CO rotational distribution described in ref 5. In the trajectories of the roaming pathways, one of the H atoms partially dissociates from H2CO to form a weakly bound radical–radical (HCO−·H) complex. Instead of dissociation of the complex into two radicals, the partially dissociated H atom roams around the HCO radical and finally abstracts the other H atom from the HCO radical. This results in the formation of the molecular products CO + H2. The roaming channel has only been recognized since 2004, is common in gas-phase reactions. The systematic prediction of pathways that follow such an unexpected mechanism is difficult when only a conventional geometry optimization approach is considered, and this is also a topic of this Perspective.

To unravel the entire photoreaction processes, a systematic characterization of the PESs of several excited states as well as the ground state is required. With the Franck–Condon (FC)
approximation, a photochemical reaction starts at the FC point on an excited-state PES. The system then goes through various reaction pathways depending on the topology of the PESs and the available excess energy. Bond rearrangements or dissociations may occur on the excited-state PES through various transition states (TSs). The system may undergo a nonadiabatic transition to a lower PES and then react on this PES. The system may cascade through several PESs via nonadiabatic transitions.

Nonadiabatic transitions take place efficiently near a seam of the intersection between two PESs.8 When the two states have the same spin and space symmetry, the intersection, called a “conical intersection”, spans an \((f - 2)\)-dimensional hypersurface, where \(f\) is the number of vibrational degrees of freedom. If the spin multiplicity or the space symmetry is different, two PESs cross in the \((f - 1)\)-dimensional hyperspace, and this termed the “seam of crossing”. The minimum-energy conical intersection (MECI) and minimum-energy seam of crossing (MESX) represent the lowest-energy structures or the critical points (or, less accurately, the “nonadiabatic transition states”) where nonadiabatic transitions take place efficiently.

To determine all of the possible photochemical reaction pathways for a given system, a systematic search of TSs, MECIs, and MESXs is required for the excited- and ground-state PESs that are accessible at a given photon energy. Figure 1 schematically illustrates the potential profiles of a three-state system. Three channels are present for the singlet first excited electronic state \(S_1\): an adiabatic reaction pathway going over a TS on the \(S_1\) surface, an intersystem crossing (ISC) path to the lower triplet electronic state through the MESX point, and a nonadiabatic pathway leading to the singlet ground electronic state \(S_0\) via the MECI point. These pathways are open when the available photon energy exceeds the energies of the corresponding critical points (i.e., TS, MESX, or MECI). ISC is slow in systems that only contain elements from the upper part of the periodic table because of the small amount of spin–orbit coupling. Transitions to a lower state may take place far from the conical intersection and the seam of the crossing regions by weak vibronic coupling and/or the emission of light, although these processes are generally slower than the three pathways illustrated in Figure 1 when these pathways are open.

Many efficient geometry optimization techniques are available for TSs, MESXs, and MECIs,9,10 and these methods require best-guess structures to initiate the search. It is extremely difficult for chemists to guess where the MECI or MESX is found. Therefore, any optimization method that requires a best-guess structure makes the determination of unexpected crossing structures difficult. A guess-free method is thus required.

Ab initio molecular dynamics (AIMD) simulations are a promising approach to the study of ultrafast photoreaction processes.11 AIMD simulations are highly desirable for studies of ultrafast nonstatistical dynamics. However, this method is extremely expensive and can be executed only for a short period (i.e., for very fast processes) for a limited number of trajectories.

To determine all of the feasible pathways, including those containing slow processes, we have developed automated reaction path search methods12,13 that constitute what we have called the global reaction route mapping (GRRM) strategy.14 These were originally developed for the TSs of the ground-state PES and have been expanded to assist in guess-free searches for the TSs, MECIs, and MESXs of different electronic states. To achieve this, we developed three approaches as briefly explained in the next section.15–17 These developments opened the door to the automated exploration of both nonadiabatic and adiabatic reaction pathways for multiple PESs. It should be noted that this approach does not explicitly consider the dynamics as well as the surface-hopping probability. The resulting discussions are thus only qualitative. Nevertheless, it is useful for a qualitative understanding of overviews of complex reaction mechanisms.

In this Perspective, we first describe our GRRM strategy for the systematic exploration of reaction pathways.14 Here we restrict ourselves to the GRRM strategy for photochemical reactions.15–17 With this strategy, we have discovered many unknown and unexpected channels for the photodissociation of small molecules.15,16,21 We first applied this method to the photolysis of formaldehyde, \(H_2CO\), which has been extensively studied experimentally and theoretically for decades, and we discovered an unknown nonadiabatic channel that involves the triplet state.15 A roaming channel on the excited electronic state PES was discovered for the first time during the photolysis of the nitrate radical, \(NO_3\).18 Moreover, unlike other roaming channels, no normal (nonroaming) channel coexists, and all of the \(O_2\) was exclusively produced via this excited-state roaming channel. In the photolysis of formic acid, \(HCOOH\), the GRRM exploration comprehensively accounted for the numerous different channels observed in various experiments.19 This result also suggests a mechanism for the conformational memory dynamics observed for the photolysis of the cis isomer of formic acid. Other application examples are also briefly introduced.20

**METHODS**

Seam Model Function (SMF) Approach. The SMF approach is a two-step procedure that allows the exploration and determination of the geometry of the MECI or MESX without a best-guess structure.15 In the first step, a search for local minima is performed using the following model function \(p_{SMF}(Q)\):

![Figure 1. Schematic of the potential energy profiles of the three states \(S_0\) (blue), \(S_1\) (red), and \(T_1\) (green). Cross and cone marks represent the MESX points between the singlet and triplet states and the MECI points between \(S_0\) and \(S_1\), respectively.](image-url)
The minimization of $F_{SMF}(\mathbf{Q})$ reveals a geometry in which both the mean energy and the energy gap are small. This is illustrated in Figure 2a, where the $F_{SMF}(\mathbf{Q})$ curve shown with the black thick line has local minima near the two crossing points between the two target states. Therefore, the minima on this function can be used as approximate MECI or MESX geometries. Because $F_{SMF}(\mathbf{Q})$ is a smooth, single-valued function, any automated local-minimum search method can be used without modification. In the second step, the approximate geometries obtained in the first step are optimized to the true MECI or MESX using any optimization method. The optimization approach in the GRRM code described below was used in our studies. It should be noted that all of the MESX and MECI structures shown below were fully optimized in the second step and have energy gaps between two target states of less than ~0.1 kJ/mol.

**Avoiding Model Function (AMF) Approach.**

The derivatives of the PES calculated by ab initio or density functional theory (DFT) methods can be discontinuous at conical intersections. Conical intersections with upper states are generally located in the high-energy regions on the ground-state PES, far from the reaction pathways. However, on the PES of an excited electronic state, conical intersections with a lower electronic state may lie below the important TSs. In some cases, even the lowest-energy point on an excited-state PES is located inside a conical intersection hyperspace. The application of automated reaction path search methods to the PES of excited electronic states is thus not straightforward. Therefore, the following model function was introduced:

$$F_{AMF}(\mathbf{Q}) = \frac{1}{2} \left[ E^{state-1}(\mathbf{Q}) + E^{state-2}(\mathbf{Q}) \right] + \frac{\left[ E^{state-1}(\mathbf{Q}) - E^{state-2}(\mathbf{Q}) \right]^2}{\alpha}$$

in which the coupling term $U(\mathbf{Q})$ is given by

$$U(\mathbf{Q}) = \frac{\beta}{2} \exp \left[ \frac{\left( E^{state-1}(\mathbf{Q}) - E^{state-2}(\mathbf{Q}) \right)^2}{\beta} \right]$$

where $\mathbf{Q}$ denotes the atomic coordinates $\{\mathbf{Q}\}$, $E^{state-1}(\mathbf{Q})$ is an adiabatic PES of the target (upper) state, $E^{state-2}(\mathbf{Q})$ is an adiabatic PES of the lower state, and $\beta$ is a constant parameter.

This expression for $F_{AMF}$ is similar to the well-known equation used for the diabatic/adiabatic transformation of two-state systems, where $E^{state-n}$ are diabatic PESs. For $F_{AMF}$, in contrast, $E^{state-n}$ are adiabatic PESs. The model coupling term $U(\mathbf{Q})$ modifies the conical intersection regions. This is illustrated in Figure 2b. The $F_{AMF}(\mathbf{Q})$ curve shown by the black thick line is smooth around the two crossing points. Any automated reaction path search method that has been developed for smooth PESs can thus be applied to $F_{AMF}$. The function $U(\mathbf{Q})$ is designed so that it has an effect only in limited regions with a small energy gap. Hence, $F_{AMF}$ is very similar to the PES $E^{state-1}$ in areas with a large energy gap, as illustrated in Figure 2b. The accuracy (i.e., how well stationary structures on $F_{AMF}$ reproduce those on $E^{state-1}$) depends on the $\beta$ value. In our experience, $\beta$ should be set to ~1/10 the vertical excitation energy. In the discussed examples, $\beta$ was set to 30 kJ/mol.

The local-minimum and TS structures on the excited-state (adiabatic) PES $E^{state-1}$ can be explored in two steps: (1) an exploration of the approximate local-minimum and TS structures as local minima and first-order saddle points, respectively, on $F_{AMF}$ by any automated reaction path search method and (2) the reoptimization of the true local-minimum and TS structures on the PES $E^{state-1}$ using the approximate structures as initial guesses. It should be noted that all of the local-minimum and TS structures discussed in this paper are fully optimized true structures on adiabatic PESs.

**Branching Plane Updating (BPU) Approach.**

On a conical intersection, there are two directions that lift the degeneracy of the two adiabatic PESs: the gradient direction (GDV) and the derivative coupling vector (DCV) direction. The plane defined by these two vectors is called the branching plane (BP), and the BP is required at every MECI optimization step to retain the geometry on the conical intersection hyperspace. The GDV is the difference between the gradient vectors of the two target states and can be readily calculated. The DCV, however, requires extra calculations. Furthermore, the DCV is not available in all ab initio theories. We thus developed an approach to estimate the BP without calculation of the DCV, using a history of the optimization steps.

We express a BP at the kth optimization step by two vectors, $\mathbf{x}_k$ and $\mathbf{y}_k$, where $\mathbf{x}_k$ is a unit vector parallel to the GDV for the adiabatic energy at the kth step and $\mathbf{y}_k$ is a unit vector on the BP perpendicular to $\mathbf{x}_k$. At the kth step, $\mathbf{x}_{k-1}$, $\mathbf{y}_{k-1}$, and $\mathbf{x}_k$ are known, and $\mathbf{y}_k$ is unknown. In the first-order approximation of diabatic PESs, the BP (i.e., the $xy$ plane) does not change by any geometrical displacement. In other words, the first-order BP at the kth step is simply the plane defined by $\mathbf{x}_{k-1}$ and $\mathbf{y}_{k-1}$. At the kth step, $\mathbf{x}_k$ is calculated exactly and may have a component not

![Figure 2. Schematic of (a) the seam model function (SMF) of eq 1 and (b) the avoiding model function (AMF) of eq 2.](image-url)
contained in \( x_{k-1} \) or \( y_{k-1} \) because of the higher-order terms obtained when determining \( x_k \) and \( y_k \) can then be estimated from the unchanged first-order BP, and such a \( y_k \) should be written as a linear combination of \( x_{k-1} \) and \( y_{k-1} \) as follows: \( y_k = s x_{k-1} + ty_{k-1} \). Because \( y_k \) is a unit vector orthogonal to \( x_k \), we obtain the following simultaneous equations for \( s \) and \( t \):

\[
\begin{align*}
    s(x_{k-1} \cdot x_k) + t(y_{k-1} \cdot x_k) &= 0 \\
    s^2 + t^2 &= 1
\end{align*}
\]

By solving eq 3, we obtain \( y_k \) as

\[
y_k = \frac{(y_{k-1} \cdot x_k) x_{k-1} - (x_{k-1} \cdot x_k) y_{k-1}}{\sqrt{(y_{k-1} \cdot x_k)^2 + (x_{k-1} \cdot x_k)^2}}
\]

(4)

This \( y_k \) is used together with \( x_k \) to construct an updated BP at the \( k \)th step, and they are saved for the next step. At the initial step, the first-order BP (x and y from the last step) is not available. A plane made of \( x_0 \) and the mean energy gradient vector was used as an initial BP. This BP is exact at the stationary points in the conical intersections because the mean energy gradient vector does not contain any components perpendicular to the BP at these points. The DCV is thus no longer necessary at every optimization step when this BPU algorithm is employed. Although this scheme in part assumes a first-order approximation, higher-order effects are taken into account by using the exact \( x_k \), and this works very well as demonstrated in numerical tests.17

**Structure Exploration and Optimization.** With the above approaches, our own automated reaction path search methods were applied for the exploration of stationary structures: local minima and TSs on the ground- and excited-state PESs as well as MECIs and MESXs between adjacent PESs. We have developed two automated reaction path search methods. In this study, the anharmonic downward distortion following12 (ADDF) method was mainly employed. Along a typical reactive potential curve, an anharmonic downward distortion (ADD) arises and increases toward a TS. Therefore, TSs and local minima beyond the TSs can be found by following the ADDs starting from a local minimum. The application of this ADDF procedure to all of the obtained local minima provides a full reaction path network including local minima and TSs on a given PES. The other automated reaction path search method called the artificial force induced reaction (AFIR) method. In the AFIR method, two (or more) fragments are pushed together by minimizing the AFIR function, which is composed of the adiabatic potential energy and an artificial force term. The minimization path of the AFIR function (the AFIR path) can be an approximate reaction path. A TS and a product for the corresponding reaction can be obtained from the AFIR path. A sufficient ensemble of the AFIR path and the resulting reaction path network can be obtained by the multicomponent algorithm13c (MC-AFIR) for bimolecular and multicomponent reactions and by the single-component algorithm13d (SC-AFIR) for intramolecular reactions. In the photochemical GRRM strategy, the ADDF and AFIR methods, which have previously been applied mainly to the ground-state PES, are applied to \( F^{\text{SMF}} \) and \( F^{\text{AMF}} \).

As discussed above, the application of ADDF and AFIR to \( F^{\text{SMF}} \) and \( F^{\text{AMF}} \) generates approximate stationary structures. These approximate structures can then be reoptimized by any standard geometry optimization method. We used a quasi-Newton method known as rational function optimization (RFO),22 implemented in the GRRM code,21 for local-minimum and TS geometry optimizations. In MESX and MECI optimizations, the gradient projection (GP) method was used. In the GP method16,h a gradient vector is recomposed as the sum of two vectors: the difference gradient between the two PESs and the projected mean-energy gradient for the two PESs. The projected mean-energy gradient is a mean-energy gradient multiplied by the projection matrix that eliminates the gradient components of degeneracy-lifting directions, i.e., the GDV in MESX optimization and the GDV and DCV directions in MECI optimization. An optimization using the recomposed gradient of the GP method thus minimizes the energy gap in these GDV or GDV and DCV directions and the mean energy on the remaining \((3N - 7)\) - or \((3N - 8)\) - dimensional hypersurface. In this study, MESX and MECI optimizations were also performed with the RFO method using the recomposed gradient of the GP method.17

**Refining Structures and Energies toward Reliable Prediction.** A third step is also required. Usually, the above-mentioned automated exploration is performed by a computationally less demanding method such as CASSCF with a small active space and basis set. All of the obtained structures are fully reoptimized at a more reliable computational level such as CASPT2 with a large active space and basis set. However, in the excited-state calculations, the dependence of the topography of the PES on the computational level is relatively large. Therefore, we sometimes face serious cases wherein the paths obtained from low-level automated searches disappear during the final high-level reoptimization process. In these cases, we locate the corresponding path manually using double-ended-type reaction path search methods such as the double-end version of the ADDF method and the locally updated plane method.23,24 We note that this manual step is the most difficult part for people who conduct these studies. As will be shown in the following examples, the automated search sometimes only provides hints about the unknown and unexpected reaction mechanisms, and a careful examination of the search output is often critically important to determine the real mechanisms.

**Summary of the Workflow.** The workflow can be summarized as follows:

(A) Application of the ADDF method to the PESs for all of the relevant electronic states to find the local-minimum and TS structures, where the AMF approach is employed in electronic excited state applications.

(B) Application of the ADDF-SMF approach to all adjacent PES pairs to find the MESX and MECI structures for the two PESs.

(C) Reoptimization of each critical point in stages (A) and (B) (obtained with a computationally less demanding method such as CASSCF) using a more reliable computational method such as CASPT2.

**Computational Program.** All of the above-mentioned approaches (i.e., SMF, AMF, BPU, ADDF, and AFIR) have been incorporated into the GRRM program and are available in the latest version (GRRM14).21 The GRRM program calls an electronic structure calculation code as an external subroutine to obtain the energy, gradient, and Hessian of the target electronic state(s) at a given geometry. Using these PES data, the GRRM program modifies the molecular geometry. In the following applications, the MOLPRO22 program was called to obtain the PES data using multireference CASSCF and CASPT2 theories. DFT calculations for the ground-state PES
and spin-flip time-dependent DFT (TDDFT) calculations for MECI optimizations were performed using Gaussian 09 and GAMESS, respectively, in combination with the GRRM program. In GRRM14, tight connectors (i.e., internally implemented interfaces) to these three quantum-chemical calculation programs are available. Furthermore, any quantum-chemical or molecular-mechanics program can be used with the GRRM code by a loose connector developed by the users.

■ RESULTS

Formaldehyde Molecule: Complex Photodissociation Mechanisms for a Simple Molecule. The first example is the photolysis of formaldehyde at relatively low photon energies (<383 kJ/mol). It was suggested experimentally that photodissociation occurs on the PES of the singlet ground electronic state \( \text{S}_0 \) after internal conversion (IC) from the singlet first excited electronic state \( \text{S}_1 \). The dynamics and reaction pathways on the \( \text{S}_0 \) PES have been studied extensively. Early studies focused on the following two channels:

\[
\text{H}_2\text{CO} \rightarrow \text{CO} + \text{H}_2 \tag{5}
\]

\[
\text{H}_2\text{CO} \rightarrow \text{HCO} + \text{H} \tag{6}
\]

For the channel shown in eq 5, the corresponding TS was determined computationally for the first time in 1974. The radical dissociation channel (eq 6) can occur both from the \( \text{S}_0 \) state and from the lowest triplet electronic state \( \text{T}_1 \), and therefore, the \( \text{T}_1 \) PES has also been studied. Additionally, a third channel, called “roaming”, also exists and was discovered in 2004. The third channel can be expressed as follows:

\[
\text{H}_2\text{CO} \rightarrow \text{HCO} + \text{H} \tag{7}
\]

where one of the H atoms, once partially dissociated, roams around the HCO fragment and finally abstracts the other H atom to generate \( \text{CO} + \text{H}_2 \). The dynamics of the partially dissociated H atom has been termed “roaming”. The remaining question concerning the low-energy photolysis was how the excited molecules reach the \( \text{S}_0 \) PES from the \( \text{S}_1 \) PES. However, knowledge about the nonadiabatic pathways has been scarce until recently. Therefore, we performed an SMF/ADDF search for the MECI and MESX structures.

Figure 3 shows a potential energy profile for the three low-lying states \( \text{S}_0, \text{S}_1, \) and \( \text{T}_1 \) of \( \text{H}_2\text{CO} \). These calculations were performed at the CASPT2 level with the full-valence active space (MS-CASPT2 for \( \text{S}_0 \) and \( \text{S}_1 \) and SS-CASPT2 for \( \text{T}_1 \)). To avoid the intruder state problem of CASPT2, a shift parameter of 0.3 was applied. In this figure, for clarity, we do not show the PES areas of the very high energy structures such as the \( \text{H}_2\text{O} \cdot \cdot \cdot \text{C} \) and related pathways as well as the pathways for the roaming channels. The molecular channel occurs through TS 2, which lies 355.7 kJ/mol above the ground state of \( \text{H}_2\text{CO} \). At 376.1 kJ/mol, the radical dissociation channel to \( \text{H} + \text{HCO} \) opens. At higher than 408.4 kJ/mol, the radical channel is also apparent from the \( \text{T}_1 \) PES through TS 13. These energetics correspond well with the available experimentally determined energy thresholds.

ISC from \( \text{T}_1 \) to \( \text{S}_0 \) was initially considered to occur in the potential well of the \( \text{H}_2\text{CO} \) form. However, in 2008, low-energy \( \text{T}_1/\text{S}_0 \) MESXs 16 and 17 were located in the potential well of hydroxycarbene in the HCOH form, and ISC was proposed to take place from this HCOH form. To visit the potential well of HCOH on the \( \text{T}_1 \) PES, the high-energy TS 14 for the 1,2-shift of the H atom must be overcome, and this was suggested to take place by quantum tunneling. In 2009 we explored the MESX and MECI points that involve the \( \text{S}_0, \text{S}_1, \) and \( \text{T}_1 \) PESs systematically by the SMF/ADDF approach. We discovered the new MESX point 12 between the \( \text{S}_0 \) and \( \text{T}_1 \) PESs.

Adopting our MESX 12, we proposed a new mechanism for low-energy photolysis as follows. After the photoexcitation, the system stays around the \( \text{S}_1 \) local minimum 21 for a long time because all of the structures connected to 21 are high in energy. The \( \text{S}_1/\text{T}_1 \) ISC takes place by trickling down from \( \text{S}_1 \) to \( \text{T}_1 \) for all of the geometries, while the molecule in the \( \text{S}_1 \) state spends a long time oscillating around 21. This occurs because the PESs for the \( \text{S}_1 \) and \( \text{T}_1 \) states have similar energies throughout the basin of 21. Although the probability at each geometry may be small because the spin–orbit coupling between the two states \( \text{S}_1 \) and \( \text{T}_1 \) that belong to the same \( \pi \rightarrow \pi^* \) electronic

Figure 3. Potential energy profiles (in kJ/mol) for the three states \( \text{S}_0 \) (blue), \( \text{S}_1 \) (red), and \( \text{T}_1 \) (green) of \( \text{H}_2\text{CO} \) at the CASPT2 level. Cross and cone marks represent MESX points for the singlet and triplet states and the MECI points for \( \text{S}_0 \) and \( \text{S}_1 \), respectively.
configuration is small, the integrated probability over a long time could be substantial. Once the system comes down to \( T_1 \) from the \( S_1 \) basin region, the \( T_1/S_0 \) ISC through the newly found MESX point 12 (391 kJ/mol) takes place within the \( H_2CO \) basin. This mechanism based on CASPT2 energetics is consistent with the result obtained by highly accurate MRCISD(Q)/aug-cc-pV5Z calculations. After the transition to \( S_0 \), the dynamics on the \( S_0 \) PES should start in the potential well of \( H_2CO \).

Our mechanism was confirmed by three-state trajectory surface hopping (3S-TSH) simulations involving the \( S_0, S_1 \), and \( T_1 \) states. In the 3S-TSH simulations, highly accurate (analytically fitted) PESs were used, and hopping between PESs was treated with Tully’s fewest switches algorithm. The 3S-TSH simulations demonstrated that the above-mentioned decay mechanism involving the \( S_1/T_1 \) trickling down and the subsequent \( T_1/S_0 \) ISC near 12 is the major process. Furthermore, a new unexpected dynamics was discovered in which the system decays to the \( S_0 \) PES and then isomerizes to HCOH on the \( S_0 \) PES before dissociation. In these trajectories, the system hopped up to the \( T_1 \) PES and then hopped down to the \( S_0 \) PES near 16 and 17. This is energetically allowed, as shown in Figure 3.

When the available energy is higher than the \( T_1 \) barrier 13 (and lower than 23), the \( H \) atom dissociation mainly takes place on the \( T_1 \) PES. This was confirmed by the sudden decrease in the HCO product’s rotational energy around the energy of 13. This is strong evidence of the involvement of the \( T_1 \) PES in the decay mechanism during low-photon-energy photolysis. If the available energy is higher than the \( S_1 \) TS 23, \( H \) atom dissociation can take place on the \( S_1 \) PES. MECI 24 is present after \( H \) atom dissociation, and the system can also reach the \( S_0 \) PES via this MECI. A symmetric CI structure that corresponds to a saddle point within the same CI is also known. CASSCF on-the-fly dynamics studies have shown that a nonadiabatic transition takes place at MECI 24 after \( H \) atom dissociation through 23, and these dynamics result in the generation of the molecular products CO + \( H_2 \) by a recombination between \( H \) and HCO. This path may be an alternative (fourth) channel that may open when the available energy is relatively high (higher than \( \sim 440 \) kJ/mol).

Some discussion has occurred about the TS of the roaming channel (eq 7). It was first suggested that no explicit TS exists for this channel. However, three different TSs that may be relevant to this channel have been reported: (1) a TS that connects 1 with 3 directly and has a structure in which the roaming \( H \) atom is in the out-of-plane direction of the HCO fragment; (2) a TS that connects 1 and 7 directly and has a structure in which the roaming \( H \) atom is in the out-of-plane direction of the HCO fragment; and (3) planar TSs for a multistep roaming path in which the roaming \( H \) atom migrates once to the \( O \) atom side of the HCO fragment and then goes back and abstracts the other \( H \) atom. Although the relevance of the second path to the roaming channel has not been discussed, we reconsidered it because the atomic movements in this path also involve long-distance \( H \) atom migration.

Figure 4 shows a reaction path network for the roaming channel of \( H_2CO \) at the CASPT2 level. Energy values (in kJ/mol) are shown near the corresponding structures. Some important bond lengths are shown in italics. Arrows are shown from TSs 30, 31, 32, 34, and 35 toward the local minima 1, 7, and 33 and the dissociated product 3. Bonds that rearrange at each TS are shown with red lines, and weak coordination bonds are shown with dotted lines. The 

![Figure 4. Reaction path network for the roaming channels of H2CO at the CASPT2 level.](image)

### Nitrate Radical: Exclusive Excited-State Roaming Mechanism

Roaming channels are known to occur on the ground electronic state and as a minor channel. However, questions arise about the possibility of exclusive roaming and whether roaming on the electronic excited state is possible. The discovery of such a case would considerably expand the generality and the importance of the roaming channel.

In 2011, for the photolysis of \( NO_3 \), we discovered an exclusive excited-state roaming channel, which breaks both of these two known rules. The photodissociation dynamics of \( NO_3 \) has been studied extensively, mainly because of its relevance in atmospheric chemistry. It has two channels:

1. \( NO_3 \rightarrow NO + O_2 \)
2. \( NO_3 \rightarrow NO_2 + O \)
The path shown in eq 8 is observed only over a very narrow wavelength range of 585–595 nm (204.5–201.1 kJ/mol), and that in eq 9 is predominant at wavelengths less than 585 nm. However, no theoretical reaction path that explains the NO + O2 channel at 585–595 nm was known until 2011. In 2010 it was shown experimentally that at 588 nm (203.4 kJ/mol) there are two pathways that give vibrationally hot and cold O2 molecules, respectively.18 A roaming path was suggested to be responsible for the generation of vibrationally hot O2 because roaming channels have previously been shown to generate vibrationally hot products as a result of the nearly barrierless recombination of two unstable fragments.7 No clear interpretation existed for the vibrationally cold product. We thus conducted SMF/ADDF and AMF/ADDF searches and discovered a highly unexpected mechanism, as discussed below.

Figure 5 shows potential energy profiles for the four states D0−3 of NO3. The profiles were obtained by MS-CASPT2/6-31+G* for D0−2 and four-state-averaged CASSCF/6-31+G* calculations for D3 with the 11 electron, eight orbital (11ε, 8o) active space.18 To avoid the intruder state problem of CASPT2, a shift parameter of 0.3 was applied. For clarity, only the important stationary points that are discussed below are shown in Figure 5. At the FC point with D3b symmetry, the degenerate D1 and D2 states are dark states and the degenerate D0 and D4 states are bright states. The 588 nm photon excites NO3 to D0/D4, and the dynamics start from D3 and D4. The molecules excited to D4 can easily move to D1 as the system is already in the intersection hyperspace at the FC point. MECI 53 between D3 and D4 is close to the FC point, and the system rapidly decreases to D2. The lowest-energy point on the D2 PES is located inside the D1/D2 conical intersection as MECI 51. The system thus moves to D1. On the D1 PES, there is no pathway that further decays to the D0 PES because the lowest MECI 46 is very high in energy and is difficult to reach with the available energy. The dissociation dynamics thus starts from D1 minimum 45 rather than D0 minimum 36.

N−O bond dissociation occurs on the D1 PES through TS 47. However, the dissociating O atom stays around the NO3 fragment and forms a weak NO3····O complex 48 on D1. In the NO2····O form, the system can move to D0 through MECI 49. Finally, an intramolecular recombination between NO3 and O takes place either on the D1 PES through TS 50 or on the D0 PES via TS 39. These pathways exhibit roaming O atom dynamics. Interestingly, the roaming dynamics involve not only the ground electronic state D0 but also the first excited state D1, in contrast to the previously reported roaming channels. Furthermore, the next-lowest TS generates the same products, i.e., 36 → 42 → 43 → 44 → 40, which is not accessible with a photon energy of 588 nm. This suggests that the NO + O2 products are exclusively generated from roaming dynamics starting at the excited electronic state D1. The discovery of this exclusive roaming channel starting from an excited electronic state breaks two known conditions of roaming: on the ground electronic state and in small fraction. This extends the significance of roaming significantly in photochemical reaction dynamics.

Our proposal was confirmed three ways. First, DFT-based on-the-fly dynamics simulations were performed, starting from the recombination TSs 39 and 50.18 The trajectory from the higher TS 50 on the D3 PES gave vibrationally cold O2, whereas vibrationally hot O2 was produced by the trajectory from the lower TS 39 on the D0 PES. These trajectories explain the generation of vibrationally cold and hot O2 as minor and major products, respectively, in the earlier experiments.45 Second, the NO A doublet propensity (correlation between the NO rotational plane and the direction of the unpaired electron) was determined by an ion-imaging experiment.46 In the recombination TSs 50 and 39, the unpaired electron is directed toward the out-of-plane direction in 50 and toward the molecular plane in 39. Therefore, the determination of the A doublet propensity is strong evidence for the involvement of these two recombination TSs. Third, extensive dynamics simulations were performed using the global PESes obtained by fitting analytical potential functions to the 90 000 MS-(17e, 13o)-CASPT2/aug-cc-pVTZ energies for D0 and D1.47 These molecular dynamics simulations starting from either 36 or 45 only gave the products NO + O2 with a roaming mechanism, and they quantitatively reproduced the experimental vibrational and rotation distributions of the products. However, the simulations did not consider the nonadiabatic transition between D0 and D1.48 The branching ratio of the NO + O2 products is not known from the simulations or from any other work. Future quantitative simulations that account for the
nonadiabatic coupling of adiabatic potentials are required for a further understanding of this system.\cite{49}

**Formic Acid Molecule: All Product Channels and Conformational Memory.** The third example is the photodissociation of the trans and cis isomers of the formic acid molecule, HCOOH. The photolysis of trans-HCOOH has been a target of many experimental and theoretical studies.\cite{50} However, the cis isomer, which easily undergoes isomerization to the lower-energy trans isomer, has been studied only in an Ar matrix.\cite{51} For trans-HCOOH, the following five channels have been observed.

\begin{align*}
\text{HCOOH} & \rightarrow \text{CO}_2 + \text{H}_2 & (10) \\
\text{HCOOH} & \rightarrow \text{CO} + \text{H}_2\text{O} & (11) \\
\text{HCOOH} & \rightarrow \text{COOH} + \text{H} & (12) \\
\text{HCOOH} & \rightarrow \text{HCO} + \text{OH} & (13) \\
\text{HCOOH} & \rightarrow \text{HCOO} + \text{H} & (14)
\end{align*}

In this section, we will show how the results of a systematic reaction pathway search can be used to assign pathways for all of the experimental reaction channels. The special topic discussed is the conformation-specific dynamics observed for cis-HCOOH upon its 193 nm photolysis in an Ar matrix.\cite{52} The CO/CO$_2$ ratios for the channels shown in eqs 10 and 11 vary dramatically depending on the initial conformation. The 193 nm photolysis of trans-HCOOH predominantly follows channel shown in eq 11 with a CO/CO$_2$ ratio of 5.0, while the photolysis of cis-HCOOH, in contrast, gives a CO/CO$_2$ ratio of 0.42. These conformation-specific dynamics are termed "conformational memory", and its mechanism has been clarified for the 1-iodopropane cation (C$_3$H$_7$I$^+$) and the propanal cation (C$_3$H$_6$O$^+$).\cite{53} However, a theoretical interpretation of the mechanism of the conformational memory in HCOOH has not been very successful. We again performed SMF/ADDF and AMF/ADDF searches and identified the origin of the conformational memory.

Figure 6 shows the potential energy profiles (in kJ/mol) for the three states S$_0$ (blue), S$_1$ (red), and T$_1$ (green) of HCOOH at the CASPT2 level. Cross and cone marks represent MESX points between the singlet and triplet states and MECI points between the two singlet states, respectively. Energies at the MRCISD(Q)//CASPT2 and UCCSD(T)//UCCSD levels are shown in parentheses and square brackets, respectively, for selected structures in a quantitative comparison with the available experimental data. The uncertainty of ±2.3 kJ/mol at MESX 72 indicates a S$_0$/T$_1$ energy gap of 4.6 kJ/mol at the UCCSD(T) level calculated for the UCCSD-optimized MESX geometry. The roaming channels that involve the partially dissociated TSs 62 and 65 in the form of HCO---OH and HCOO---H, respectively, are shown with dashed lines.

**Figure 6.** Potential energy profiles (in kJ/mol) for the three states S$_0$ (blue), S$_1$ (red), and T$_1$ (green) of HCOOH at the CASPT2 level. Cross and cone marks represent MESX points between the singlet and triplet states and MECI points between the two singlet states, respectively. Energies at the MRCISD(Q)//CASPT2 and UCCSD(T)//UCCSD levels are shown in parentheses and square brackets, respectively, for selected structures in a quantitative comparison with the available experimental data. The uncertainty of ±2.3 kJ/mol at MESX 72 indicates a S$_0$/T$_1$ energy gap of 4.6 kJ/mol at the UCCSD(T) level calculated for the UCCSD-optimized MESX geometry. The roaming channels that involve the partially dissociated TSs 62 and 65 in the form of HCO---OH and HCOO---H, respectively, are shown with dashed lines.
clear explanation was available for this 259 nm threshold. Our interpretation, based in Figure 6, is that this threshold is related to MESX 72. From the S1 minimum of 74, there is no accessible stationary point at lower than 462 kJ/mol except for 75 and 76 for the trans/cis isomerization. It is thus expected that the S1/T1 ISC occurs from 74 to 66 and from 75 to 67 with a trickling mechanism (without going through crossing), as is the case for formaldehyde. The S1 PES is very close to the T1 PES in the basin of HCOOH, and long residence allows slow S1/T1 ISC to take place inside the HCOOH basins. After the S1/T1 ISC, MESX 72 is the lowest gateway that escapes from the T1 minima 66 and 67. Moreover, the calculated energy value of 462.2 kJ/mol for 72 is very close to the experimental threshold. After the S0/T1 ISC through MESX 72, the system predominantly undergoes molecular dissociations on S0 to give CO + H2O (via TS 57) and CO2 + H2 (via TS 59) because of their low barriers.

The experimental quantum yield of the HCO + OH channel (eq 13) is virtually zero below 475 kJ/mol (252 nm), and it gains intensity with an increase in the excitation energy. This threshold is reproduced well by T1 TS 69. Figure 6 shows that the other OH dissociation channel opens at 498.6 kJ/mol on the S1 PES through TS 77. Because the ISC is a slow process, the direct OH dissociation on the S1 PES will be dominant if the available excess energy is sufficient to overcome barrier 77 on the S1 PES. The OH dissociation channel was observed to be dominant at 222 nm (539 kJ/mol) with an OH product quantum yield of ~0.80. This is consistent with the experimental observation wherein different OH generation dynamics were observed for excitation energies of 244 nm (490.3 kJ/mol) and 230 nm (520.1 kJ/mol). MECI 78 is present for the partially dissociated HCOO·····OH geometry. This MECI is close to the roaming pathway through TS 62 on the S0 PES. After the nonadiabatic transition, CO + H2O may be produced via the roaming OH dynamics.

The COOH + H generation channel (eq 12) opens at 472.4 kJ/mol via T1 TS 71. A similar dissociation channel from the S1 PES requires much higher excess energy (not shown in Figure 6 for clarity). This is consistent with a hydrogen (Rydberg) atom photofragment translational spectroscopy study, which showed that this channel occurs exclusively on the T1 PES. In this experiment, it was also found that the HCOO + H channel (eq 14) is on the S1 PES, and the required energy was estimated to be ~532 kJ/mol. As shown in Figure 6, this channel opens through S1 TS 80. The barrier at 541.4 kJ/mol is in qualitative agreement with the experimental estimate of ~532 kJ/mol. A similar dissociation channel from the T1 PES needs higher excess energy (not shown in Figure 6 for clarity), which is consistent with the experimental result. After dissociation through TS 80 and the subsequent nonadiabatic transition through MECI 81 at the partially dissociated HCOO·····H geometry, the roaming dynamics for the generation of the molecular products CO2 + H2 may occur through S0 TS 65.

In summary, on the basis of our calculation results, all of the low-photon-energy photodissociation channels of trans-HCOOH observed to date and their mechanisms can be explained as follows. Between 462 and 472 kJ/mol, two successive ISCs from S1 to S0 via T1, followed by the molecular channels shown in eqs 10 and 11 on the S0 PES are dominant. At 472 kJ/mol, a C–H bond dissociation channel (eq 12) opens on the T1 PES. At 475 kJ/mol, an OH dissociation channel (eq 13) from the T1 PES becomes accessible. Above 499 kJ/mol, a direct OH dissociation channel (eq 13) on the S1 PES becomes dominant. Above 541 kJ/mol, a direct O–H bond dissociation channel (eq 14) becomes available on the S1 PES. Overall, these results that were obtained by a systematic exploration of stationary structures are consistent with all of the experimental data. This result is highly encouraging for the future use of our photochemical GRRM strategy in combination with a proper quantum-chemical calculation method and kinetic theory for the prediction of elemental reaction channels for use in atmospheric modeling.

The remaining question is that of the conformational memory observed upon the 193 nm (620 kJ/mol) photolysis of cis-HCOOH. Figure 7 shows potential energy profiles that provide a possible answer to this question. The S0−3-MS-CASPT2/aug-cc-pVDZ was applied to the S1/S0 MECIs 84 and 86; S0−3-MS-CASPT2/aug-cc-pVDZ to the S1/S0 MECIs 82, 83, and 85 and to the S2 energy at the FC point; and S0−3-MS-CASPT2/aug-cc-pVDZ to the other structures, all with a (10e, 8o) active space. During this photolysis, a total energy of 637.5 kJ/mol relative to trans-HCOOH is available. The photolysis was postulated to occur starting from the S1 PES. Searches for the stationary structures as well as molecular dynamics simulations have been performed on the S1 PES. However, it is obvious from Figure 6 that isomerization from the cis isomer to the trans isomer occurs rapidly on the S1 PES through a very low barrier of only 2.0 kJ/mol. In molecular dynamics simulations, this isomerization was found to occur immediately after photolysis. Thus, explanations of the conformation-specific dynamics for cis-HCOOH have not been successful in previous theoretical studies.

We found the S0/S1 MECIs 82 and 83 in the weakly interacting HCOO·····H region with the partially dissociated H
atom in the cis conformation with respect to HCOO. After the nonadiabatic transition at MECI 82, the system settles to the S2 PES, and barrierless H atom abstraction from the HCOO part by the partially dissociated H atom in the HCOO−→H complex occurs. This results in the generation of the molecular products CO2 + H2. Through MECI 83, a barrierless recombination between HCOO and H gives vibrationally highly excited cis-HCOOH. After the recombination, the excess energy localized in the O−H bond vibrational mode is expected to prefer, although not exclusively, a molecular dissociation to CO2 + H2 on the S2 PES starting from the FC geometry increased the O

This section discusses the dissociation on the S2 PES and two successive nonadiabatic transitions at MECI 82 and 83. Important, S1/S2 MECI 84 and the S1/S0 MECIs 82 and 83 that led, without barrier, to the H2 + CO2 products contain the partially dissociated H in the cis conformation with respect to the HCOO hydrogen, and the two H atoms in the cis position can form a bond to dissociate as CO2 + H2.

The 193 nm (620 + 17.5 kJ/mol) photon energy is not enough to reach the S2 PES at the FC geometry. Nevertheless, a fraction of the molecules can reach the S2 PES with this photon energy at geometries slightly deviated from the FC point. Furthermore, the oscillator strength of 0.0362 for the S0 → S1 transition at the FC point is much larger than the oscillator strength of 0.0009 for the S0 → S1 transition at the MS-CAS(10e, 8o)-PT2/aug-cc-pVDZ level for the four lowest singlet states.

A similar path for trans-HCOOH also leads to H atom dissociation on the S1 PES and two successive nonadiabatic transitions through S1/S2 MECI 86 and S0/S1 MECI 85. This results in the H + HCOO products as well as the regeneration of the S0 minimum 54 to maintain the trans conformation. In the trans conformation, the two hydrogen atoms are too distant to form the H2 + CO products. The S2 path for trans-HCOOH is expected to be less important compared with cis-HCOOH because the excitation energy from S0 to S2 at the FC point for trans-HCOOH is substantially larger than that for the cis isomer.

Finally, our mechanism that involves rapid O−H bond dissociation on the S1 PES is consistent with the other two cases that have been observed for 1-C3H7I+ and C2H5O+ and involve an ultrafast descending process on the excited-state PES.52 In the actual experiment,51 the complete dissociation of the H atom on the S1 PES can be prevented by an Ar matrix. Thus, QM/MM simulations considering the effects of surrounding Ar atoms explicitly by MM force fields53,54 are encouraged for a further understanding of the dynamics.
discussed. The SMF approach allows a systematic search for MESX and MECI structures in combination with local-minimum sampling methods that have been applied to the ground-state PES.\textsuperscript{15} With the AMF approach, the automated exploration of local-minimum and TS structures on the excited electronic state PESs can be performed using the automated reaction path search methods developed for the ground-state PES.\textsuperscript{16} Furthermore, the BPU method allows the accurate determination of MECI points without DCV calculations.\textsuperscript{17} These approaches have realized the automated exploration of photoexcitation pathways.\textsuperscript{18−20}

In our studies, the ADDF method was used for initial structure exploration.\textsuperscript{21} In this step, CASSCF or CASPT2 with a small active space and basis set was adopted to reduce the computational cost. The topography of the excited-state PESs may change significantly depending on the choice of theoretical level. Therefore, the pathways obtained by the initial automatic search at a low theoretical level have to be confirmed using a higher-level theoretical method. This procedure has been most difficult and still requires sufficient knowledge about the excited-state chemistry. Nevertheless, the initial automatic and unbiased search provides many useful hints that would not be available otherwise and has led to the discovery of unexpected reaction mechanisms, as demonstrated and discussed above.

The above-mentioned results are highly encouraging for the theoretical prediction of elementary reaction channels for atmospheric modeling. Many unknown features of photo-dissociation reactions have been found for several important photochemical reactions by the use of the GRRM strategy. We plan to use the present strategy and code for future challenges in this and related areas.

We again emphasize that the present approach is useful for a qualitative understanding of reaction mechanism overviews. For roaming pathways, quantitative discussions are difficult when only traditional TST-like simulations based only on local-minimum and saddle-point geometries are considered.\textsuperscript{7} For the quantitative prediction of branching ratios, reaction time scales, and product energy distributions, among others, molecular dynamics simulations that account for the coupling of adiabatic potentials are recommended.

Our interest has recently been expanded to the study and design of photofunctional molecules for applications such as bioimaging, photoswitching, and photosensitizers using the GRRM strategy. The structures and energies of the MECIs and MESXs determine the efficiency of nonadiabatic transitions that are closely related to the functionality of these molecules. In complex photofunctional molecules, many MECIs and MESXs are expected to exist for various distorted structures. The presented unbiased and untargeted search will allow the identification of the kinds of molecular distortions that cause crossing and thus quenching, such as rotation around double bonds and out-of-plane distortions of conjugated structures. This theoretical information is difficult to obtain otherwise, and opportunities are thus provided to control and design more efficient photofunctional molecules.

For this purpose, we have combined the SMF approach with TDDFT.\textsuperscript{55} One of the most serious drawbacks of TDDFT is that it cannot describe the conical intersection between the reference ground state and the first excited state with the same spin and space symmetry.\textsuperscript{56} This problem has been eliminated by spin-flip TDDFT (SF-TDDFT).\textsuperscript{57} SF-TDDFT can be used for the optimization of the geometries of MECIs between these states.\textsuperscript{58} We have thus developed an efficient, automated MECI explorer by combining the SMF approach, SF-TDDFT, and SC-AFIR.\textsuperscript{59} This combined approach is currently being used in practical applications such as the analysis and design of photofunctional molecules containing 30−50 atoms.

## ASSOCIATED CONTENT

* Supporting Information

Full citations for refs 25 and 26. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

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## REFERENCES


