

Excursion, Roaming and Migration of Hydrogen Atom during Dissociation of Formaldehyde

Hyung-Rae Kim

Department of Chemistry, Hankuk University of Foreign Studies, Kyonggi-do 449-791, Korea. E-mail: hyung2@hufs.ac.kr
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Several interesting features in trajectory were observed in the direct dynamics study of formaldehyde dissociation above radical dissociation limit. The hydrogen atom deliberately placed on the radical dissociation path can turn around at some distance from C without completion of dissociation and return to HCO moiety, colliding with it just as in a radical-radical recombination and producing a highly energized molecule. Excursion of a hydrogen atom to a distance of 6-8 bohrs and migration of a hydrogen atom back and forth between C and O are two of the most interesting features exhibited by the energized molecule. A series of excursions is seen to lead to a different kind of dissociation resembling roaming-like dissociation characterized by high vibrational excitation of H₂ fragment. It is suggested that excursion occurs due to involvement of two different force field systems that exhibit discontinuity in 6-8 bohrs from HCO moiety. We argue that roaming is a non-zero impact parameter version of the excursion.

Key Words : Excursion, Roaming, Migration, Trajectory

Introduction

Recently formaldehyde dissociation has been a hot focus of experimental and theoretical/computational work due to discovery of roaming as a new path of dissociation.¹⁻¹¹ Several other molecules are also known to dissociate *via* roaming path.¹²⁻¹⁹ Roaming-induced dissociation seems to have acquired a status of generality in molecular dissociation. Quasi-classical trajectory (QCT) calculations employing highly accurate potential energy surface have offered explanations for the product energy distribution²⁰ for roaming-induced dissociation. QCT calculations have shown that the roaming hydrogen atom abstracts the other hydrogen atom in the HCO moiety from a relatively large distance, leading to a high vibrational excitation of the resulting hydrogen molecule (early barrier argument) and a low rotational excitation of CO fragment (impulsive release argument).⁶ However it is still not clear why a hydrogen atom roams. Is it a universal phenomenon? What characteristic features of potential energy surface are responsible for roaming? Is roaming a marginal phenomenon that only occurs near radical dissociation limit? Are other behaviors possible than roaming under similar conditions? In order to provide answers to these questions it would be necessary to look more closely into trajectories of formaldehyde undergoing dissociation (radical and molecular) under controlled conditions.

Most existing trajectory studies have concentrated on obtaining information about product energy disposal by running many trajectories starting from highly vibrationally excited formaldehyde molecules in order to simulate experimental conditions. Individual trajectories were visualized only to show the existence of roaming and abstraction. Even though roaming has been observed for energies higher than the radical dissociation limit, it would be interesting to run

trajectories at even higher energies for two reasons. First, at high energies three isomers of formaldehyde and saddle points connecting those equilibrium structures are energetically accessible and many interesting trajectories are expected to appear. Secondly, it would be interesting to see what happens when a trajectory is forced to start on a radical dissociation path by providing a hydrogen atom with appropriate initial momentum and enough energy to move it at least 10 bohrs away from C atom along the radical dissociation path. Momentum components for one or both of the hydrogen atoms can be varied to adjust their initial directions of movement. Total energy needs to be set well above radical dissociation limit. The energy and momentum are assigned values so that the hydrogen atom does not dissociate completely but to return to HCO producing highly excited formaldehyde due to insufficient amount of energy to escape (called aborted radical dissociation). Initial conditions are chosen carefully so as to prevent the trajectory from being trapped in the usual molecular dissociation path. We are especially interested in observing the behavior of the returned hydrogen atom in the collision complex obtained by the collision of the returning hydrogen atom with HCO moiety.

In this paper computational details and choice of initial energy and momenta are described in the computational details section. In the results section several interesting behaviors of the trajectories that were observed will be explained. The results will be analyzed using characteristic features of the potential energy surface, especially in connection with excursion/roaming.

Computational Details

Trajectories were computed using BOMD (Born-Oppen-

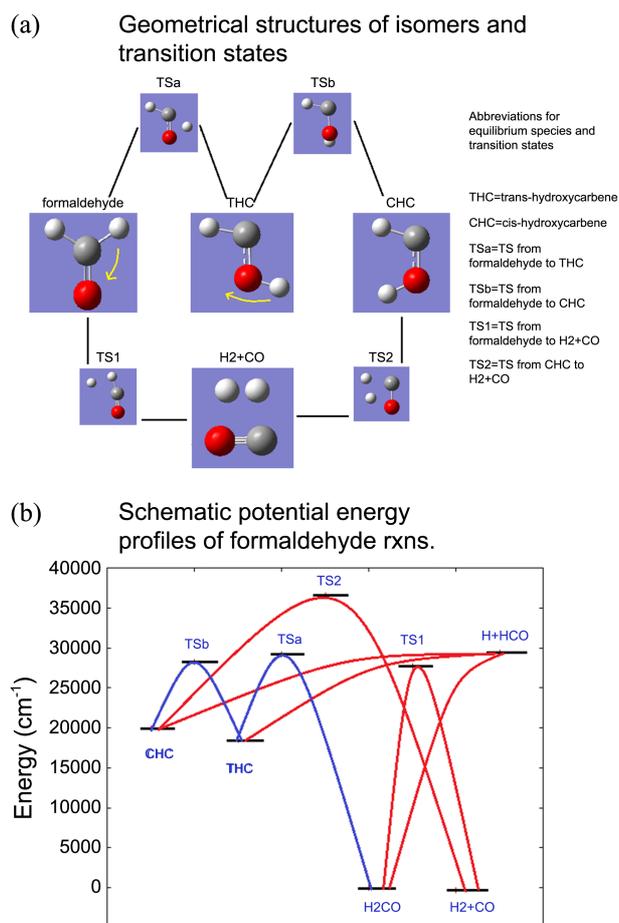


Figure 1. (a) Schematic potential energy profiles. (b) Reactions of formaldehyde system.

heimer molecular dynamics),²¹⁻²⁵ a direct dynamics method incorporated in Gaussian 09 package.²⁶ B3LYP hybrid functional of density functional theory was used with 6-311G(2d,p) basis set. The choice of model chemistry and basis set was made to accommodate both accuracy and practical feasibility. Geometry optimization and frequency calculations were done for all equilibrium species (formaldehyde, *cis*-hydroxycarbene and *trans*-hydroxycarbene) and the relevant transition states involved in the trajectory. Calculated geometrical structures are shown in Figure 1(a). Schematic potential energy profiles connecting various equilibrium species and transition states are shown in Figure 1(b). Energies calculated with B3LYP/6-311G(2d,p) were in reasonable agreement with energies obtained with multi-reference method and more extensive basis set (CASPT2/cc-pvtz²⁷) except for TSb, where discrepancy is quite high (Table 1). Geometrical structures optimized using the CASPT2/cc-pvtz were similar to B3LYP/6-311G(2d,p) structures shown in Figure 1(a). Relaxed scans of R(C-H), where all geometrical variables except for each R(C-H) are optimized, were performed using both methods. Potential energy profiles for the relaxed scan were similar to each other for R(C-H) less than 7.0 bohr. All trajectories were calculated using B3LYP/6-311G(2d,p) for practical reasons. Since

Table 1. Relative energies of equilibrium species, transition states and dissociation products. These have been calculated using the same level of DFT calculation (B3LYP/6-311G(2,p)) as used for trajectory calculations. CASPT2/cc-pvtz results are given in parentheses for comparison

Relevant species (Isomers, transition states, dissociation products)	Energy in cm ⁻¹ relative to H ₂ CO (zero point energy corrected)
THC (trans-hydroxycarbene)	18561.3 (18456.9)
TSb (TS for CHC ↔ THC)	28281.1 (42119.6)
CHC (<i>cis</i> -hydroxycarbene)	19948.6 (19989.6)
TSa (TS for H ₂ CO ↔ THC)	29216.6 (29105.6)
TS2 (TS for CHC ↔ H ₂ + CO)	36528.0 (36647.9)
H ₂ CO (formaldehyde)	0.0 (0.0)
TS1 (TS for H ₂ CO ↔ H ₂ + CO)	27735.4 (28311.2)
HCO + H (radical dissociation products)	29851.5 (28073.1)

B3LYP calculations were unreliable at large R(C-H), the portions of the trajectories at large R(C-H) were not used in analysis.

Direct dynamics method is very convenient for calculating and visualizing individual trajectories. Instead of using normal mode sampling, atomic coordinates and mass-weighted velocities are directly specified in the input. Trajectories are stopped using usual stopping criteria in which the completion of molecular dissociation is checked by plotting the relative recoil velocity of fragments with respect to time (completion of dissociation process is indicated by the constant relative recoil velocity, namely the disappearance of interaction between the fragments). Numerical accuracies in integrations are adequate since total energy is conserved for most of the trajectories up to about 3000 fs, within which most interesting behaviors occur. GaussView program²⁸ was used to visualize the trajectory during a run to check if initial mass-weighted velocities of hydrogen atoms that were specified in the input file were indeed guiding correctly the movements of hydrogen atoms toward the intended direction.

Instead of simulating experimental conditions, we wished to investigate the behaviors of trajectories during critical moments before dissociation. Therefore trajectories are started from a configuration obtained by distorting conventional transition state¹ slightly toward the reactant (formaldehyde) configuration. The starting configuration is chosen so that initially it does not lie on the intrinsic reaction coordinate (IRC) path of the conventional MD *via* the skewed planar transition state (TS1). The potential energy of the starting configuration (PE = -114.4083 a.u.) is lower than that of TS1 ($E_{TS} = -114.4050$ a.u.) by 0.0033 a.u. We ran trajectories with $E > E_{RD}$ where E_{RD} is the radical dissociation limit (-114.3919 a.u.). In order to have $E > E_{RD}$, kinetic energy (KE) greater than 0.0164 a.u. needs to be supplied. KE is varied by assigning different values to the components of mass-weighted velocities (hence components of linear momentum vectors) for atoms. For most trajectory runs kinetic energies for two hydrogen atoms are varied while those of C

and O atoms are fixed.

Results and Discussions

Most trajectories run at initial conditions as specified in the previous section eventually lead to dissociation. Before dissociation many interesting behaviors have been observed. Depending on energy and initial momenta assigned to hydrogen atoms, large amplitude vibrations (LAV), excursions, migrations and dissociations (molecular and radical) are observed in combination or independently. At low energies (still higher than the RD limit) LAV, excursions and MD *via* TS1 are prevalent whereas at high energies aborted RD, excursions, migrations, MD *via* TS1, MD *via* TS2, MD induced by excursion and RD are more common.

Most of these interesting behaviors are observed in those trajectories where the hydrogen atom departing from HCO moiety at the early stage of the trajectory fails to dissociate completely and makes a return trip back to the HCO moiety. Namely, we use this aborted radical dissociation (RD) as a means of causing a high speed collision of a hydrogen atom with HCO. It is relatively easy for a hydrogen atom to get on an RD path because it involves just an elongation of an H-C bond to a certain distance. Even though RD, a simple bond fission reaction, proceeds without having to overcome a potential barrier, it is not a one-way event towards radical products. Once the hydrogen atom gets on the RD path with sufficient energy, it will encounter no potential barrier ahead towards the completion of dissociation process. However when its energy of escape is in short supply in later stage of its trip to RD, the RD may not be completed. Energy exchange occurs among various degrees of freedom while energy is pumped into or out of potential energy pool during the progress of RD process. The energy imparted to the relative translational motion of the departing hydrogen atom along the RD path may not be sufficient for letting it escape completely from HCO moiety. In other words internal degrees of freedom of HCO may be drawing more of its share from the available energy than translational energy of H as the hydrogen atom recedes from HCO moiety. The exhaustion of escape energy by the hydrogen atom will of course hinder its forward movement and make it return at some point back to HCO moiety. We have been calling this phenomenon as aborted RD and used it as a way of simulating a recombination collision of radicals for the observation of various interesting behaviors. The returning hydrogen atom acts as if it were travelling toward the HCO moiety for a bimolecular collision with low impact parameter. The returning hydrogen atom is accelerated as it approaches HCO moiety and shows many interesting behaviors such as LAV, excursion, migration of a hydrogen atom and eventual dissociation (molecular or radical).

Energy Dependence of Trajectory Behaviors. We first describe change of behaviors with increasing initial energy, which is, the sum of quantum mechanically calculated potential energy of the initial geometry ($PE = -114.4083$ a.u., fixed) and chosen kinetic energy. For $E_{TS} < E < E_{RD}$,

trajectories run from our initial geometrical configuration (TS1 distorted slightly toward the direction of formaldehyde) fail to get on the RD. It does not take MD path either because the configuration is off TS1 or momenta of hydrogen atoms are not directed toward IRC of MD *via* TS1. Even for $E > E_{RD}$, MD *via* TS1 does not occur easily if the energy is low. Below ~ 0.06 a.u., large amplitude vibration (LAV) is most frequent for many trajectory runs and no MD is observed. Above $KE = 0.06$ a.u., MD begins to appear after a varying period (100 fs-1000 fs) of LAV. Figure 1(a) shows internuclear distance vs. time plot for a trajectory run at $KE = 0.07617$ a.u., showing LAV before MD. In that Figure LAV by the hydrogen atoms (H1 and H2) has three segments: LAV by H1, LAV by H2 and LAV by H1 again. The vibrational amplitude of C-H stretch tends to increase with total energy. At higher energy ($KE = 0.1054$ a.u.) the LAV coexists with an interesting type of motion by a hydrogen atom. A hydrogen atom (called H1) makes a trip outward on the RD path up to 6-8 bohrs from HCO moiety before returning. We call this type of behavior 'excursion' instead of very large amplitude vibration (Figure 1(b)). An excursion certainly cannot be called a vibration because H2, the hydrogen atom on HCO moiety, executes many periods of vibration during one excursion period of H1, the hydrogen atom on an excursion. Excursion is more like pseudo-dissociation than vibration. Excursions occur in almost all trajectories run at $KE > 0.7$ a.u. In Figure 2(b), it is seen that H1 reaches maximum extension of 6-8 bohrs from HCO, which we will call 'excursion peak' in internuclear distance vs. time plot. For some trajectories run at even higher energies, the hydrogen atom can travel past the excursion maximum along the RD path but it usually fails to dissociate completely. As it returns without accomplishing RD, it hesitates for a brief period at the excursion maximum before entering formaldehyde valence force field. In Figure 2(c) ($KE = 0.1516$ a.u.), the shoulder on the return path of H1 occurs at the same distance (6-8 bohrs) from HCO as for an excursion peak. It is thus like a half-excursion. In Figure 2(c) the returning H1 is seen to execute two more full excursions and many periods of LAVs before MD.

At much higher energies migration of a hydrogen atom from C to O leads to the formation of THC *via* a transition state (TSa). The migration of H can continue to CHC. The CHC can dissociate into the same molecular products (H_2 and CO) as formaldehyde. It occurs *via* a new transition state (TS2). TS2 is a cyclic planar transition state, a configuration distorted from CHC toward molecular products. Examples of migrations, formation of THC and CHC, and MD (*via* TS1 or TS2) will be shown later when we discuss details of those behaviors.

We call MD after a sequence of LAV/excursion/migration a delayed molecular dissociation (abbreviated as DMD) in contrast to fast molecular dissociation (FMD), which is an MD without delay. The DMD can be considered as a special kind of complex mode dissociation.

A hydrogen atom departing on its second or later attempt for radical dissociation may eventually be successful. In this

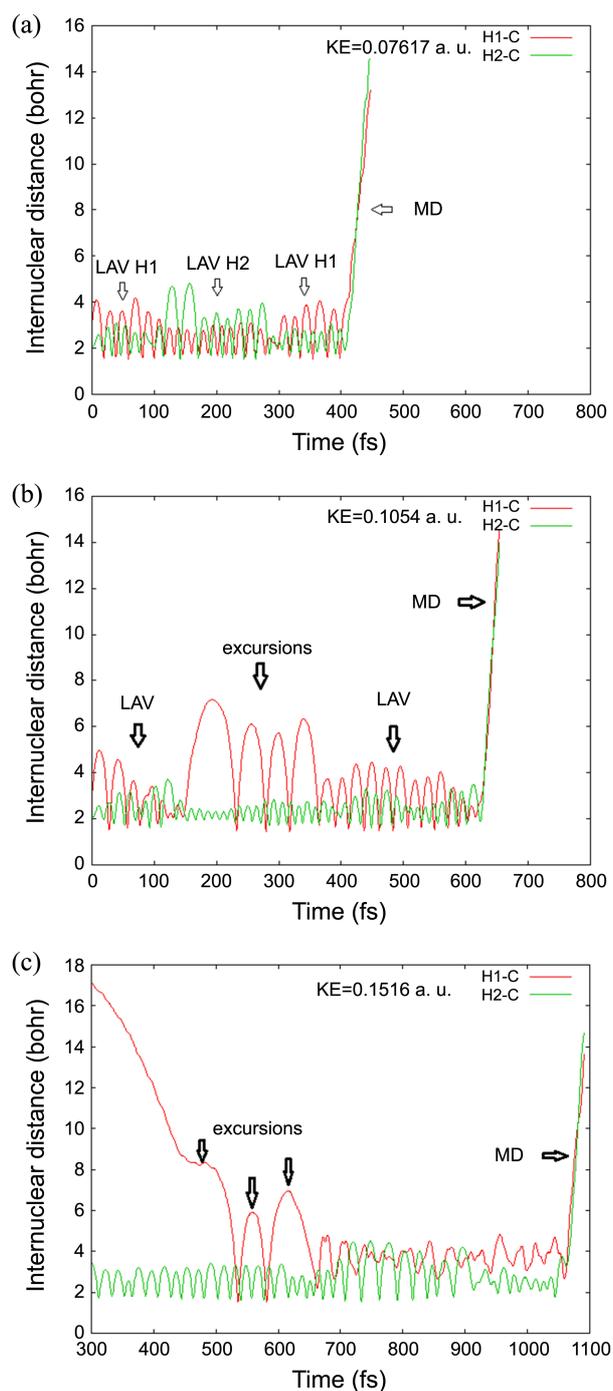


Figure 2. H-C distance change with time. (a) LAV by H1 → LAV by H2 → LAV by H1 → MD *via* TS1. (b) LAV → excursion → LAV → MD *via* TS1. (c) Aborted RD → excursion → LAV → MD *via* TS2.

case the radical dissociation is a delayed event (we call this a delayed radical dissociation, DRD). The energy range where DMD and DRD occur appears to overlap to some degree, even though the DRD occurs at higher energy range than the DMD does. The behaviors of DRD and DMD trajectories before dissociation are similar. They involve single or multiple excursions, migrations, LAVs, *etc.* When total energy is much higher than the RD limit, the hydrogen atom cannot

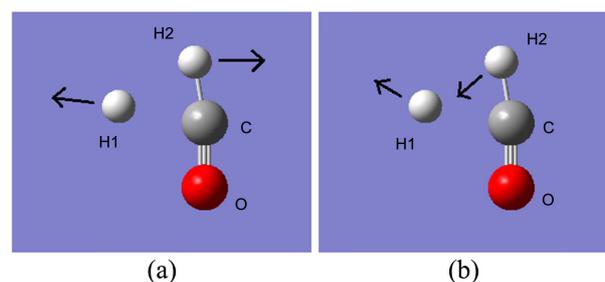


Figure 3. Momentum directions of hydrogen atoms and initial geometry for (a) delayed MD/RD and (b) direct MD *via* TS1.

make a return trip and dissociates completely at its first attempt. This is the case of fast radical dissociation (called FRD).

In the next subsections we will discuss excursion, migration and roaming in more detail.

Excursion and Migration. Direct molecular dissociation with no delay (FMD) can be made to occur readily even when a trajectory is started from off-TS1 configuration. FMD can be made possible by directing hydrogen atoms toward MD path with $E_{\text{tot}} > E_{\text{RD}}$ (Figure 3(b)). However if momenta of hydrogen atoms are directed toward RD path (Figure 3(a)) instead of toward MD, the hydrogen atom with outward momenta (H1) will start out on an apparent RD path. Namely, H1 starts to move away from C as if it were dissociating. In Figure 3(a) it is shown that H1, the hydrogen atom on excursion, is given outward initial momenta away from C while H2, the hydrogen on HCO moiety, is given initial momenta away from the direction of C-H1 bond.

If H1 does not possess sufficient recoil energy for the RD, it loses most of outward momentum at a certain distance far from C and returns to HCO moiety due to strong long-range attraction. The returning hydrogen atom collides with HCO moiety and exhibits many interesting behaviors. After the collision, excursion by a hydrogen atom to a maximum travel distance of 6-8 bohrs is the most common behavior shown by the hydrogen atom (see Figure 4). Excursions usually appear as a train of multiple excursion peaks. Excursion is qualitatively different from LAV where a hydrogen atom travels only up to about 5 bohrs from C atom. The excursion will later be related with well-known ‘roaming’ trajectories. At the farthest distance of a given excursion H1 can stand almost still for some time (for example, about 40 fs for the first excursion in Figure 4) before making a return trip. We abbreviate as X the geometrical configuration at the maximum extension of an excursion peak and treat it, for convenience, like a chemical species when a sequence of events is described for a trajectory. During the lifetime of X (the duration of time when H1 is at a near standstill), the relative translational energy of H with respect to HCO is almost zero while the rest of available energy is partitioned to internal degrees of freedom of HCO moiety. As the returning H1 approaches HCO moiety, its relative translational energy (and hence relative speed) increases because it is moving toward a deep potential well. At the end of the return trip, all

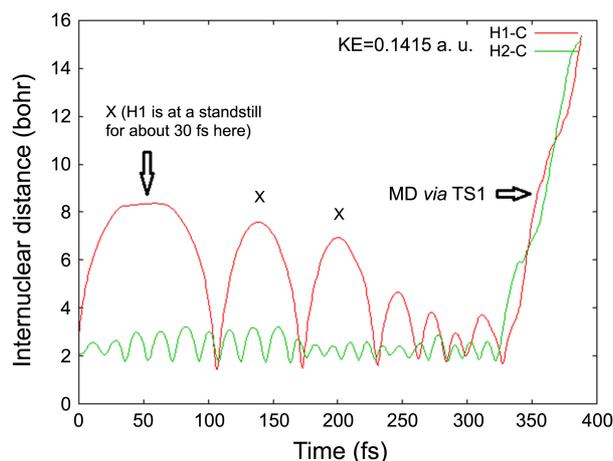


Figure 4. Multiple excursions before MD. Note the standstill by H1 in the first excursion for about 30 fs. The species X denotes the configuration at maximum H1-C distance for a given excursion. X is defined only for the purpose of description of reaction scheme.

the relative translational energy is either converted to internal energy of formaldehyde (or one of its isomers) or is used as recoil energy for another excursion. The return trip follows closely but not exactly the same path as the outgoing path.

It is also seen from Figure 4 that an excursion period contains 3-6 periods of the other H-C stretching vibration.

Excursion has the following distinct features. It has a unique maximum extension range, which is 6-8 bohr. One excursion peak (by H1) can contain 2-6 periods of H2-C stretch vibration (Figure 4). It can be easily distinguished from large amplitude vibration (LAV), which has maximum travel distance in the range of 2-5 bohrs (see Figures 2(a) and 2(b)) and mostly one-to-one correspondence between H1-C and H2-C vibrations. Excursion appears usually as a train of 2-4 peaks even though single excursion peak does exist. An excursion sometimes experiences a brief standstill period before returning (Figure 4). An excursion peak can appear as a shoulder at the return stage of an aborted RD (Figure 2(c)). Excursion-induced molecular dissociation (EIMD), which will be elaborated on later, produces highly vibrationally excited H_2 molecule whereas MD *via* TS1 or MD *via* TS2 do not. All of these observations indicate that excursion is an independent entity, clearly distinguished from LAV.

When a hydrogen atom returns from an aborted dissociation, it usually bonds to the same C atom that it started its initial outward trip from. This is due to very small initial orbital angular momentum possessed by the departing hydrogen atom. Thus the returning H atom is involved in a local mode vibration initially before being transformed to a normal mode vibration later. Thus we now have a highly vibrationally excited H_2CO molecule. The hydrogen atom on a return path that is off the initial path (due to finite impact parameter) may miss C atom and bond to nearby O atom. It is also possible that one of the hydrogen atoms in highly energized formaldehyde can break its bond to C during a highly excited HCH bending vibration and form a

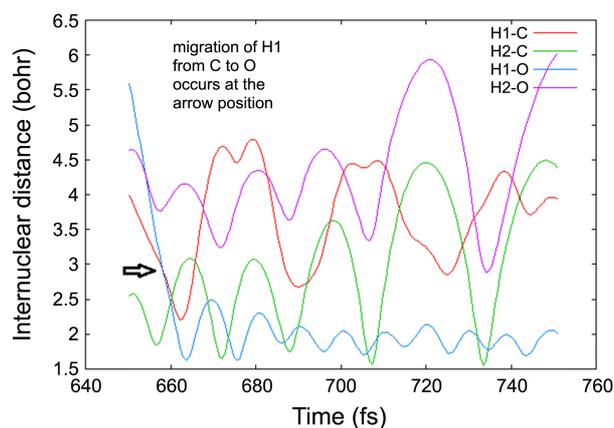


Figure 5. Expanded view for 650-750 fs window for the trajectory in Figure 1(c). Note the migration of H1 from C to O, decrease of H1-O vibration (purple) amplitude and increase of H2-C vibration (green) amplitude after migration.

bond to nearby O atom. We will call this change of bond from C-H to O-H (or *vice versa*) 'migration'. Initial migration results in formation of highly vibrationally excited *trans*-hydroxycarbene (THC) *via* a transition state, called TSa. THC can also be formed when the returning H atom bonds directly to O atom. While executing LAV, the H atom on O atom of THC can move around O atom to the opposite side of C-O axis and form *cis*-hydroxycarbene (CHC) *via* a transition state (called TSb). The H atom may continue its migratory motion and bond to C again. Thus the cycle $H_2CO \rightarrow THC \rightarrow CHC \rightarrow (THC) \rightarrow H_2CO$ constitutes a one full round of orbiting of H around HCO. Note that the change from CHC to H_2CO must go through intermediate THC stage (in parentheses), which is formed by flipping of non-orbiting hydrogen to the other side of C-O axis. Migration portion of a trajectory (Figure 2(c)) is expanded and redrawn in Figure 5. Crossing of H1-C and H1-O curves occurs at the position indicated by an arrow. This is the moment of migration of H1 from C to O atom, forming THC. THC and CHC usually undergo isomerization to each other several times before MD from TS2. The LAV by O-H in THC or CHC continues for about 400 fs before eventual MD *via* TS2 in Figure 2(c).

TS2 is a cyclic transition state, which connects CHC to molecular products ($H_2 + CO$). Its energy (-114.3636 a.u.) is much higher than RD limit. The dissociation *via* TS2 occurs from CHC only. Even though RD is possible from THC, MD is impossible from THC configuration. THC has to be isomerized to CHC in order to undergo MD *via* TS2.

It is also interesting to note that no excursions occur by the hydrogen atom bonded to O atom (in THC or CHC), even though successful or aborted RD's can occur from them.

Figure 6 shows a series of snapshots for a trajectory where migrations lead to formation of THC and CHC and MD from CHC *via* TS2 leads to formation of molecular products. First, H atom migrates from C to O, forming THC. Then it goes around O atom to the other side of C-O axis, forming CHC. MD *via* TS2 occurs near the last stage of the

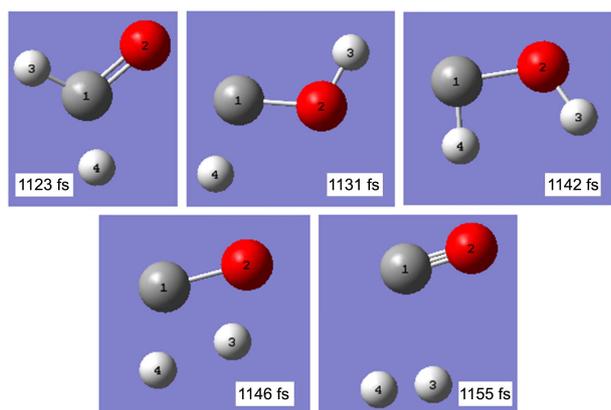


Figure 6. Snapshots of a trajectory showing the formation of THC, CHC and MD *via* TS2. 1123 fs: aborted RD returns to H₂CO, 1131 fs: migration to THC, 1142 fs: migration to CHC, 1146 fs: nearest approach to TS2, 1155 fs: dissociating into H₂ and CO.

trajectory. The hydrogen atom on O atom forms a chemical bond to the other hydrogen atom on C atom *via* a cyclic transition state (TS2) instead of migrating to C.

Excursion-induced Molecular Dissociation (EIMD). The hydrogen atom on an excursion can abstract the other hydrogen atom from HCO moiety. This is a totally different type of MD. The nascent H₂ fragment is highly vibrationally excited because internuclear distance between the two hydrogen atoms is quite large when abstraction starts. In Figure 7, the hydrogen atom (H2) in the third excursion peak is seen to be detached from C (denoted as H abstraction in Figure 7) and begins to form a bond to the other hydrogen atom (H1) and moves away as a unit from CO. We call this type of dissociation excursion-induced dissociation. In many trajectories exhibiting excursion-induced dissociation, the dissociation is preceded by several excursions. The fact that not every excursion leads to dissociation would indicate that a certain condition has to be met in order for the dissociation to be successful. Visual investigation of a particular ex-

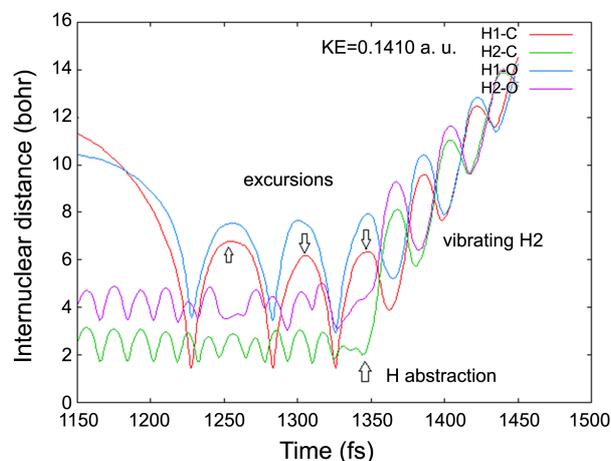


Figure 7. A typical EIMD trajectory. The sequence of behaviors: Return of H1 from aborted RD → two short excursions → dissociation of H₂ (KE = 0.1410323 a.u.) (Only 1150-1450 fs window is shown).

cursion-induced dissociation (Figure 7) shows that H₂ rotates around C to face the incoming H1 before being detached from C and attached to H1 to begin the molecular dissociation process. The flat portion in R(H₂-C) just before the arrow (next to 'H-abstraction' label in Figure 7) corresponds to this half-rotation before H₂ formation.

A series of excursions just before MD in Figure 7 would correspond to conventional roaming if the hydrogen atom had non-zero angular momentum. The vibrational excitation of H₂ (32.8% of available energy) for the trajectory in Figure 7 is quite high, which is what one would expect for a typical roaming-induced dissociation. The abstraction of H₂ by H1 starts at 1345 fs where $R_{H1-C} - R_{H2-C} = 4$ bohrs, which is quite large. For this particular trajectory rotational excitation of H₂ is extremely high (59.4%), while relative recoil energy is very small. Even though we were not able to run sufficient number of trajectories to get statistically meaningful product energy distribution, high vibrational/rotational excitation of H₂ appears to be most frequent for this kind of trajectories.

Interpretation of Excursion/EIMD in Terms of Potential Energy Surface. The occurrence of excursion may be related to a possible existence of a discontinuity in force field system a hydrogen atom experiences as it recedes from or returns to HCO moiety. Namely, the existence of a kind of force field boundary located at 6-8 bohrs from HCO moiety could be the cause of the excursion behavior. Consider a hydrogen atom on a pseudo-dissociation path making a return trip toward HCO. Attractive dispersive force field, typical for radical-radical interactions, would be dominant at large distances. At short distances a strong chemical (valence) force field would be superimposed. Thus a boundary may exist at a certain distance of H and HCO. In the boundary region interactions between H1 and H2, H1 and C and H2 and C coexist. A potential barrier appears to exist because incoming H1 is seen to find difficulty penetrating inside the boundary (shoulder type of excursion) and also because outgoing H1 fails to cross the boundary into the RD path (full excursion peak). The hydrogen atom at the boundary stands still for a while or roams about the HCO moiety.

We now look into the details of excursion process. If the incoming H1 can overcome the barrier it will cross the boundary into the strong H₂CO force field and continue its motion toward HCO. A fast approaching hydrogen atom may not be affected by the presence of a small barrier. However a slow approaching hydrogen atom may hesitate for a brief period at the boundary before entering a different type of force field due to balance between attractive and repulsive forces arising from discontinuity of force field (see, for example, the shoulder at 450 fs in Figure 2(c)). In a similar manner a translationally hot hydrogen atom going on an excursion can escape from H₂CO force field easily and travel outside of the force field boundary toward complete dissociation or aborted RD. In contrast a low speed hydrogen atom may fail to cross the boundary due to insufficient outward momentum and a high potential barrier to dissociation. It will turn back at 6-8 bohrs from C without escaping from the attractive well (see, for example, the

excursion peaks in Figures 2(c) and 4).

Excursion is frequently repeated several times before changing to other behaviors such as aborted RD, migration, LAVs, etc. A train of excursion at times leads to MD, producing H₂ and CO products just as for MD *via* TS1 or MD *via* TS2. However this type of MD does not appear to involve any prominent transition state (Figure 7). Also the nascent H₂ is highly internally excited. A single, isolated excursion does not usually lead to such MD. We call this type of MD as excursion-induced MD. The formation of H₂ occurs by abstraction of a hydrogen atom (H₂) belonging to HCO moiety by the hydrogen atom at the force field boundary. A hydrogen atom, H₁, standing still for a brief moment at the boundary, appears to have an ability of remotely abstracting H₂ when a certain condition is met. Normally H₂ would resist being abstracted because it is involved in a vibrational motion deep inside a potential well of HCO. However, if H₂ were positioned on its path to dissociation (HCO → H + CO), the possibility of abstraction of H₂ by H₁ would increase. In other words the radical dissociation of HCO within HCO force field might assist H₁ sitting on the boundary with abstracting H₂. The visualization of the excursion-induced dissociation clearly shows it. The details of the dissociation process will be described in the ensuing work.²⁹ This remotely controlled abstraction (as opposed to contact abstraction) of H₂ within the HCO force field by H₁ standing at the boundary would correspond to excursion/roaming-mediated MD. Since equilibrium bond distance of H₂ is short, the remotely controlled abstraction is expected to cause a high vibrational excitation of H₂. When the direction of linear momentum of incoming hydrogen atom (H₁) is different from that of outgoing hydrogen atom (H₂), the newly formed H₂ molecule will rotate. The degree of rotational excitation of H₂ will depend on their relative directions.

Excursion vs. Roaming. Much similarity exists between excursion and roaming. The roaming trajectories observed by Bowman and coworkers were obtained using randomly sampled initial conditions of formaldehyde, whereas our trajectories were directed purposefully toward radical dissociation path and were started from a single pre-determined configuration. For our trajectories excursion and return were approximately along the line of centers of H and HCO moieties, the impact parameter for the collision of H with HCO being near zero. Orbital angular momentum of the incoming hydrogen atom for those trajectories is so small that the hydrogen atom will tend to penetrate into HCO force field instead of roaming about the HCO moiety. Trajectories that have larger orbital angular momentum do show roaming. Very short period of roaming is actually observed at the maximum travel distance of an excursion (Figure 4) or as a form of a shoulder during the return path of an aborted RD (Figure 2(c)). Thus it can be said that roaming takes the form of an excursion in our trajectories. The dissociation followed immediately by an excursion (Figure 7(b)) has much in common with roaming induced dissociation. Abstraction of a hydrogen atom from 6-8 bohrs from C and high vibrational

Force fields and trajectory behaviors

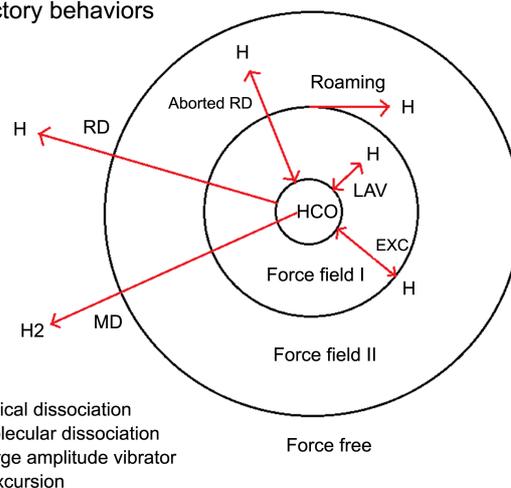


Figure 8. Schematic for proposed mechanism of roaming trajectory.

excitation of H₂ clearly indicate that if trajectories were run at high impact parameters, they should be of the same kind as observed by Bowman group.

Both excursion and roaming occur at about the same distance from HCO moiety, which would indicate that they occur under the same force field. In contrast to the hydrogen atom on an excursion the roaming hydrogen atom, which has a large angular momentum and a small radial momentum, will move mostly in the non-radial directions instead of making a return trip to HCO moiety after a short standstill at the maximum travel distance. Roaming can occur when the net radial force on the hydrogen atom on excursion is close to zero near 6-8 bohrs away from HCO moiety. At this distance attractive radial force on the hydrogen atom may be balanced by repulsive radial force. When a hydrogen atom possessing angular momentum enters this region of balance of force, it can jump out of its initial radial track and wander in the non-radial direction, executing a very complex, roaming (sometimes wobbling) motion. During the roaming motion the hydrogen atom will try to maintain a distance of about 6-8 bohrs. Since the roaming of hydrogen atom is a result of a balance between attractive force and repulsive force at about 6-8 bohrs from HCO moiety, a slight change

Schematic diagram of reactions

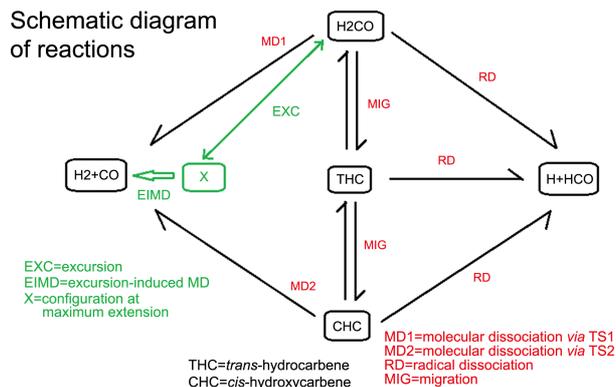


Figure 9. Schematic of formaldehyde dissociation.

in initial condition can make a roaming disappear. In Figure 8 a schematic diagram is shown, where roaming is shown to be occurring at a boundary between two different force field systems.

Conclusions

By using direct dynamics method we have observed many interesting modes of trajectories before dissociation of formaldehyde, when trajectories were started close to but off the TS1 saddle configuration and directed toward radical dissociation path at energy higher than radical dissociation limit. Figure 9 shows schematic diagram of reactive and nonreactive processes along with chemical species involved. The diagram includes processes such as inter-conversions among isomers (H_2CO , CHC, and THC), excursion to X, radical dissociation (RD), molecular dissociation (MD), *etc.*

Excursion and migration are two of the most important features of our trajectories. Excursion is almost ubiquitous in our trajectories. Excursion has a maximum extension of 6-8 bohrs. It usually appears as a train of 2-4 peaks. It sometimes appears as a shoulder in the return portion of an aborted RD. Short period of standstill at the maximum extension can appear. Excursion can be thought as a special kind of roaming. Excursion induced dissociation produces a highly vibrationally excited H_2 molecule just as a roaming dissociation does.

Migration is also a frequent event in our trajectories. Migration can occur when highly excited H-C-H bending vibration in H_2CO pushes one of the hydrogen atoms toward O atom. Then the trajectory crosses over the potential barrier (called TSa) to trans-hydroxycarbene (THC). THC can also be formed when the hydrogen atom returning from an excursion misses C atom and bonds directly to the neighboring O atom. Migration can continue from THC to *cis*-hydroxycarbene (CHC) *via* the transition state TSb and further to H_2CO , completing a cycle. Molecular dissociation can occur from H_2CO (*via* TS1) or from CHC (*via* TS2), while radical dissociation can occur from any one of the three isomers.

Dissociation, molecular or radical, is delayed due to excursion and migration. Both DMD and DRD usually involve one or more aborted RDs, trains of excursions, migrations, *etc.*

MDs occur *via* two different transition states. The most frequently occurring MD is a MD1 *via* TS1 (skewed formaldehyde configuration of C_s symmetry), while MD2 *via* TS2 (cyclic transition state obtained by distortion of *cis*-hydroxycarbene) was observed less frequently. When total energy is higher than all potential barriers (TS1, TS2, TSa, and TSb), many possible combinations of species and pathways are possible due to re-visits and most of them have been observed in our trajectory studies.

The complex behaviors of trajectories before dissociation and the variety of reaction modes are due to the ease of migration by the hydrogen atom and to the existence of several equilibrium structures obtained by the migration. The ease of migration is due to high energy that is released

to internal degrees of freedom of formaldehyde by the hydrogen atom returning from an aborted RD to a low potential energy basin. The high internal energy can cause re-excursion or migration. Migration is needed for TS2 dissociation because MD *via* TS2 is only possible from CHC, which can only be reached by migration. Thus migration can make a trajectory visit the part of the phase space that may be difficult to access from formaldehyde configurational space. Unless energy is extremely high molecular dissociation is usually the eventual sink of a trajectory.

We have shown that an excursion is just a low impact parameter version of roaming. A large impact parameter (or high orbital angular momentum) by the hydrogen atom returning from an aborted RD would make it roam rather than make it undergo excursion. We have also shown that a train of excursions can lead to formation of H_2 and subsequent separation of H_2 from CO. We have called this kind of dissociation excursion induced molecular dissociation (EIMD). In EIMD, H_2 vibration was highly excited. We argued that the EIMD appeared to be assisted by the partial dissociation of the hydrogen atom (H_2) from HCO during its abstraction by H1. For the explanation of the phenomena of excursion and EIMD we have suggested a possible existence of discontinuity in potential energy surface near R(H_2 -C) of 6-8 bohrs, which will be elaborated in our next work.²⁹

In this work we concentrated on the dynamics of formaldehyde before dissociation. Detailed dynamics during the dissociation process needs to be investigated in order to completely understand the whole dynamics of formaldehyde dissociation. In particular we would like to investigate whether trajectories actually pass by closely or skirt around the known transition states (TS1 or TS2) or other possible transition state. We certainly would like to know what potential terrain a roaming trajectory travels in during dissociation process. These will be dealt with in the next article.²⁹

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Supporting Information. AVI files for typical trajectories.

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