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Excited State Carbene Formation from UV Irradiated Diazomethane

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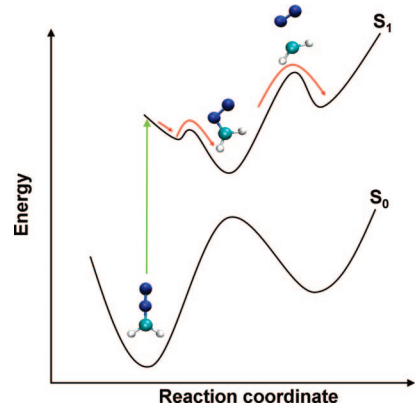

The laser flash photolysis process of diazomethane has been studied by using a real time propagation time-dependent density functional theory (RTP-TDDFT) combined with molecular dynamics. The activation energy barrier for disintegrating diazomethane into nitrogen (N_2) and carbene (CH_2) molecules significantly decreases in the electronic excited S_1 state compared to that in the S_0 ground state. Furthermore, the produced carbene molecule can be in the electronic excited state of $^1CH_2$ ($^1B_1$) instead of the lowest state among singlet states $^1CH_2$ ($^1A_1$), which is evident in the wave function characteristics of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) throughout the disintegration. This is regarded as the initial stage of the rearrangement in the excited state (RIES), the evidence of which has been given by experiments in the past decade. In the RIES mechanism scheme, we suggest that the photoreaction in the S_1 state contributes considerably to the photochemistry of carbene formation. The passing near the S_1/S_0 conical intersection, which allows the transition to ground state diazomethane producing the lowest singlet state carbene molecule, is considered a rare event from our molecular dynamics, although this has been regarded as the dominant mechanism in previous theoretical studies.

Introduction

The origin of the difference between photolysis and pyrolysis products through carbene formation raises the fundamental question about the pathway of carbenic photoreaction. For example, methylethyldiazirine (MED) in Scheme 1 shows different relative product yields depending on the reaction methods.[1] A reactive intermediate, methylethylcarbene (MEC), can be formed and undergoes hydrogen migration for the final product. Since the products through photolysis have relatively higher yields for unstable isomers, like α-butylene, *cis*-β-butylene, and isobutylene rather than the most stable *trans*-β-

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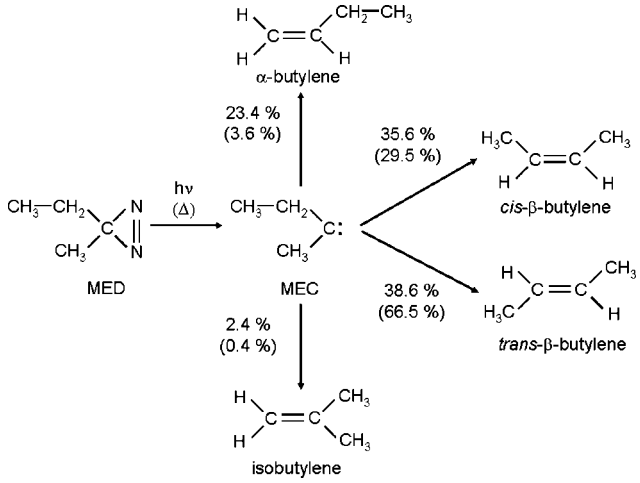
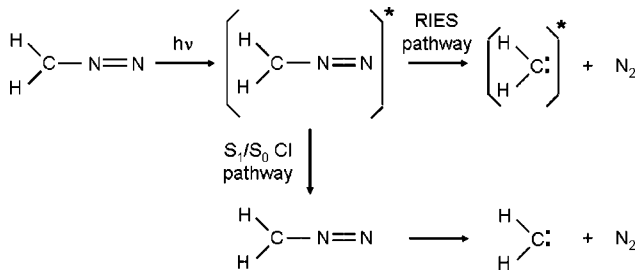
SCHEME 1. Photolysis and Pyrolysis of Methylethyldiazirine through Carbene Formation[a]



[a] Upper and lower numbers are the relative product yield through photolysis and pyrolysis, respectively.

SCHEME 2. Carbene Formation and Its Pathways



butylene, it was explained that MEC is vibrationaly hot for overcoming the activation barrier for the corresponding H-migrations. It was also reported that a similar relative product yield was observed for different kinds of diazirines and diazomethane, repeating the fundamental question.[2] Therefore it is essential to clarify the carbene formation and its pathway to the final product, as shown in the right-hand side of Scheme 2 for instance.

To answer this fundamental question, the rearrangement in the excited state (RIES) mechanism was proposed by Platz et al. and has been supported by other groups.[3−10] Carbene precursors, such as diazirines or diazomethanes, which consist of carbene and N_2 molecules, are electronically excited when irradiated with ultraviolet light. It has been argued whether N_2 extraction in the electronically excited states of the carbene precursors can produce electronically excited carbene and lead to hydrogen migration in these states. Since the corresponding activation energy barrier in the excited state can be different from those in the ground state, the RIES mechanism supplies a plausible explanation of the photochemical process.

Recent experiments gave supporting evidence of the RIES mechanism. Platz et al. performed laser flash photolysis experiments on carbene precursors: *p*-biphenylyldiazoethane (BDE) and *p*-biphenylydiazomethane (BDM).[8] Both molecules have *p*-Biphenyl radicals, which are relatively stable for hydrogen migration after carbene formation. For other radicals in carbene, CH_3 and H are expected from the BDE and BDM molecules. The ultrafast laser absorption spectra for identification on a subpicosecond time scale showed similar results in BDE and BDM. The only difference was a 40% decrease of the 450-nm peak for BDE. Since the corresponding carbene has a CH_3 radical, which induces isomerization of the carbene by hydrogen migration in the RIES mechanism, the decrease in absorption spectra can be regarded as a contribution of hydrogen migration. The ultrafast laser absorption spectroscopy results are consistent with kinetic studies on the RIES mechanism. From these studies, the product yield from the RIES mechanism is estimated to be considerable.[9,10]

Contrary to these experiments, computational studies have argued against the RIES mechanism for diazirines, the isomer of diazomethane, one of the simplest carbene precursors.[11−13] Compared with the RIES mechanism, which suggests the possibility of a photochemical reaction from the formation of electronically excited carbene, previous computational studies with multiconfiguration self-consistent field (MC-SCF) calculations and complete active space self-consistent field (CASSCF) calculation suggest that carbene is formed in the singlet ground state by S_1/S_0 conical intersection (CI). As is shown in Scheme 2, photoexcited diazomethane has two pathways. One is the RIES pathway and the other is the S_1/S_0 CI pathway. Although the experiments suggest that the RIES pathway for the photochemistry is from excited carbene formation, previous computational studies insist that the S_1/S_0 CI pathway is dominant and the RIES pathway is most likely not. To the best of our knowledge, computational support for the RIES pathway has not yet been reported. Thus, a study on the RIES pathway in photolysis with use of a different theoretical method is necessary.

We present a study on the real-time propagation time-dependent density functional theory (RTP-TDDFT)[14−16] on the excited carbene formation of methylene from photoexcited diazomethane. In comparison with previous computational studies,[11−13] our calculations show the direct formation of excited $^1CH_2$ ($^1B_1$) supporting the RIES mechanism. Instead of the S_1/S_0 CI pathway, which is rare according to the current simulation, a decrease in the activation energy barrier to dissociate N_2 in the S_1 excited state of diazomethane is important. We discuss that the quantum yield of the excited carbene formation is dependent on the wavelength of the excitation laser, and the formation of excited carbene can be one of the processes in the RIES mechanism.

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Computational Details

We used the RTP-TDDFT approach[14,15] to investigate the photochemical reaction of diazomethane. Instead of the well-known linear response time-dependent density functional theory (LR-TDDFT), nonperturbative RTP-TDDFT methods are used for taking into account nuclear motions and the associated nonlinear effects. The motions of nuclei were treated classically. Our simulations were performed with an RTP-TDDFT code called First Principles Simulation Code for Electron Ion Dynamics (FPSEID),[15] where Ehrenfest-type dynamics of nuclei as well as electronic states propagation can be carried out[16] with an updated Suzuki−Trotter-type split-operator method.

For the preparation of the initial state of the RTP-TDDFT simulation, we adopted a photon picture of light in conjunction with the electronic band structure to prepare an approximated Franck−Condon state. We regarded the laser pulse as a bunch of photons and assumed that Franck−Condon vertical excitation from the ground state to an excited state takes place instantaneously by absorbing a single photon. We first calculated the singlet ground state. The S_1 state of diazomethane from the Franck−Condon vertical excitation was attained by promoting one of the two electrons occupying the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). In this way, we prepared the singlet S_1 state of diazomethane as the initial state. We did not consider the S_2 state of diazomethane since its energy is far from the excitation energy of the photon in the experiments.[3−10]

We used the so-called *adiabatic* approximation for the exchange-correlation energy functional. The Perdew−Zunger-type parametrization[17,18] for conventional DFT was used. Soft norm-conserving pseudopotentials were used to express the interactions between valence electrons and ions.[19,20] The cutoff energy of the plane wave basis set for the Kohn−Sham orbitals was set to 60 Ry. The Γ point was used for calculating the diazomethane molecule in the gas phase. We adopted a cubic supercell with a length of 10 A under periodic boundary conditions. Visual molecular dynamics (VMD) graphic packages were used for the artwork.[21]

Since no carbene formation appeared in the dynamics from the S_1 Franck−Condon state with no initial kinetic energy of ions, there should have been an activation energy barrier for carbene formation in the excited state. To estimate the upper bound of the activation energy barrier, we artificially imposed velocities on the carbon and nitrogen atoms to enhance the dissociation of N_2. The total kinetic energy imposed on the system was 2 eV.

According to experiments in the reference, the photolysis process can be enhanced with higher excitation energy of laser. The excitation with higher energy can be interpreted as transition to high mode vibronic state which has higher kinetic energy than the 0−0 transition state. In that case, the enhancement of photolysis with higher excitation energy implies that there can be an activation barrier and the higher excitation energy help to overcome it. The imposed velocities technique is introduced to mimic the transition to higher vibronic state above the Franck−Condon transition state. The value of 2.0 eV is just tentative and for measurement of the upper-bound of the activation barrier height, which was small enough compared to the corresponding quantity under the electronic ground state. That was why we did not test other kinetic energies.

TABLE 1. Geometrical Parameters of Ground and First Excited States of Diazomethane[a]

	C−N	N−N	C−H	C−N−N	H−C−H
			ground state		
exp[b]	1.32	1.12	1.08	180	127
FPSEID	1.29	1.14	1.08	180	124.6
MC-SCF[c]	1.30	1.14		180	
CASSCF[d]	1.320	1.140	1.065	180	126.1
			S_1 state		
FPSEID	1.28	1.22	1.11	180	117.0
CASSCF[d]	1.366	1.202	1.072	180	121.9

[a] Internuclear distances are given in angstroms and bond angles in degrees. [b] From ref 18. [c] From ref 12. [d] From ref 11.

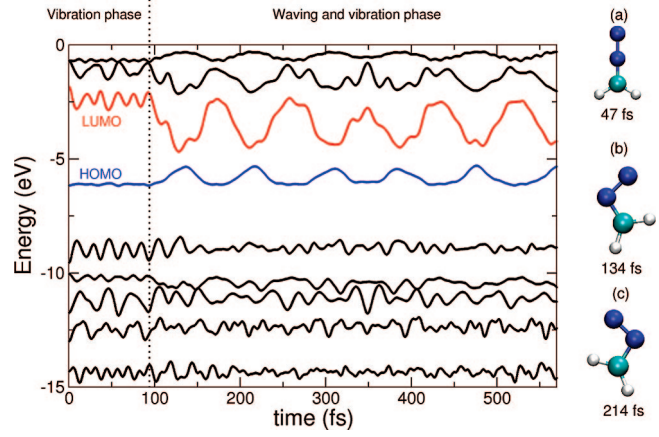

FIGURE 1. Trajectories of expected values of Kohn−Sham orbital energies and selected snapshots of molecules. Horizontal and vertical axes are time in fs and energies in eV, respectively. Half-occupied HOMO and LUMO levels are signified by red and blue lines, respectively. The vertical dotted line differentiates two phases of motions. See movies 1 and 2 in the Supporting Information for the two phases of motion.

Results and discussion

The calculated results for the ground state are consistent with the experiments and previous calculations, which adopted MC-SCF and CASSCF. The geometrical parameters of the ground and the first excited state in our calculations are shown in Table 1 along with the results of other calculations. As shown in Table 1, our results show quite reasonable agreement with the experiments and previous calculations. As for the first excited state, our results show consistency in that (1) the C−N−N chain is elongated (2), the C−H bond length is elongated, and (3) the H−C−H angle is reduced compared to those of the ground state. The wave function characteristics of the states, including HOMO and LUMO, are also consistent with those of the CASSCF calculations. In agreement with CASCF calculations, HOMO and LUMO self-consistently determined from our DFT calculations also demonstrate n and π^* character of molecular orbitals, as can be seen in Figure 4.

For the Franck−Condon transition energy, we deduced the photoexcitation energy of S_0−S_1 transition by calculating the difference in the total energies between the first excited singlet

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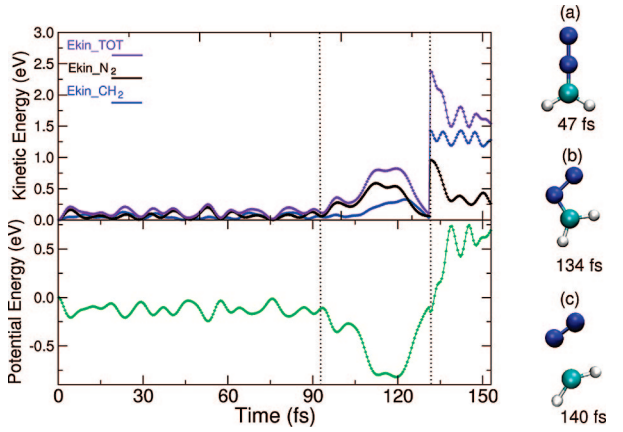

FIGURE 2. Trajectories of kinetic energies and potential energy. The kinetic energies of total N_2 and CH_2 are shown in the upper left panel of the graph. The vertical dotted lines differentiate the motion phases of stretching, bending, and dissociation. At the time of the right vertical dotted line, kinetic energies were imposed on the carbon and nitrogen atoms in the C−N bond in the opposite direction. The characteristic points of motions are shown with three molecular structures on the right. The potential energies are relative to the energy of the S1 Franck−Condon state. See movie 3 in the Supporting Information for the dissociation process.

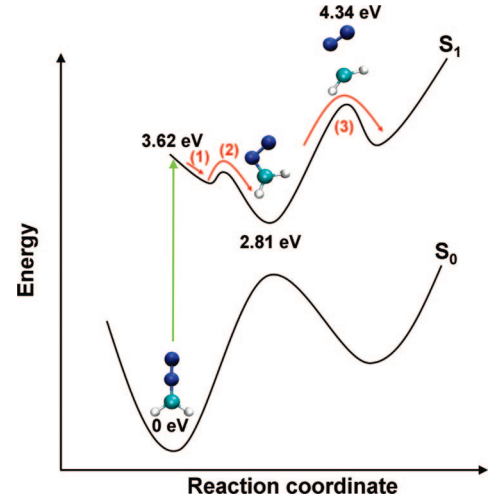

FIGURE 3. Schematic picture of the carbene formation reaction. The black solid lines represent S_0 and S_1 potential energy surfaces. Three different motion phases and the corresponding energies relative to the ground state energy are shown. The green arrow represents the Franck−Condon transition. The red arrows indicate the time line of the carbene formation reaction.

state and the ground state. The resulting photon wavelength was 344 nm (3.6 eV), which was comparable to previous calculations. Arenas et al. reported that the energy difference between the S_0 ground state and the S_1 is 390 nm (3.18 eV) in the CASSCF level.[11] Since the S_0−S_1 Franck−Condon transition energy is larger than the 0−0 transition energy, we calculate the corresponding energy for the direct comparison. Although our result of 373 nm (3.32 eV) obtained from DFT calculations deviates from that of the more accurate CASPT2 level,[11] it is comparable with CASSCF calculations. Arenas et al. assume that the Franck−Condon excitation state immediately goes to the minimum in the S_1 potential energy surface, which is lower than the Franck−Condon energy state, suggesting that our calculations show good agreement with the previous one.[11] Yamamoto et al.'s results also are consistent with ours in these geometries.[10]

Our RTP-TDDFT simulation on the S_1 potential energy surface of diazomethane showed two different vibration phases and approached near the S_1/S_0 CI. The trajectory of expected Kohn−Sham orbital energies and selected snapshots of the molecular structure are shown in Figure 1. After the Franck−Condon transition, the motions of diazomethane showed a C−N−N stretching mode, which changes into a combination of bending (814 cm^{-1}) and stretching modes (2124 cm^{-1}). The corresponding wavenumbers were obtained by the Fourier analysis of potential change throughout the simulation along with the time-axis. It is noticeable that the calculated frequency of stretching mode shows quite good agreement with experiments (NN stretch mode 2087−2115 cm^{-1}).[22] After ∼95 fs, the molecule starts to wave bend the C−N−N angle with all atoms in the same plane. To clearly show the molecular motion, three selected snapshots are given on the right of Figure 1. Note that the half-filled HOMO and LUMO levels become close in energy throughout the bending and vibration motions. Snapshots with closer HOMO−LUMO levels correspond to the bent molecular structures, two of which are shown on the right of Figure 1, b and c.

Compared with S_1/S_0 CIs of previous works,[11−13] our RTP-TDDFT calculation shows that the S_1/S_0 CI is a rare event and the system remains in the S_1 potential energy surface in high probability. For the S_1/S_0 CI, the HOMO and LUMO levels should have the same energy, but this was not the case in our calculation despite the similarity in the molecular structure between that of previous works[11,12] and ours. In previous theoretical works, N_2 was extracted after the radiationless deexcitation to the S_0 state through the S_1/S_0 CI. In the RTP-TDDFT simulations, radiationless deexcitation was detected by the appearance of off-diagonal elements of Hamiltonian and high-frequent oscillation in the expectation values due to the Rabi oscillation between the S_1 and S_0 states.[15,23] However, the appearance of off-diagonal elements of Hamiltonian and radiationless deactivation from complete matching of the half-filled HOMO and LUMO states did not appear in our RTD-TDDFT calculations. To make sure of this, we carried out the simulation up to 570 fs with no bias in the ionic motions showing no significant difference. However, it does not exclude the possibility of S_1/S_0 CI completely since it might occur at a larger time scale. We conclude that nonadiabatic transition through the CI is rare and motions of nuclei do not take the system to the exact conical intersection with considerable probability. Therefore, the important factor should not be the nonradiative decay of the S_1 state into the S_0 state, but the remaining activation barrier for N_2 dissociation on the potential energy surface of the S_1 state. To estimate the energy barrier in the S_1 state, we adopted the imposed velocities technique. The carbene formation time, including N_2 extraction, was less than a subpicosecond, as shown in previous state-of-the-art experiments.[7,8] Since our simulation of the S1 state did not show N_2 extraction within that time scale, there could be an activation energy barrier to extracting N_2. To estimate the barrier of the S_1 state in the RTP-TDDFT scheme, we imposed velocity to

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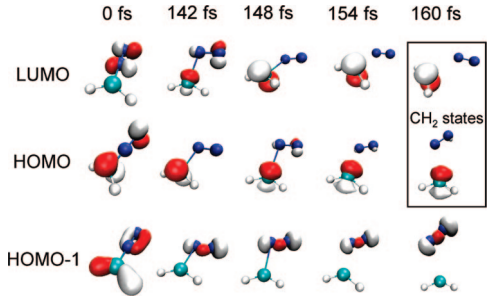

FIGURE 4. The wave function characteristics at selected times. The red and white spheres represent wave function isosurfaces of the same magnitudes of positive and negative values. The n and π^* states of diazomethane changed to σ and π states of CH_2 as N_2 was extracted. The rectangular area shows the formation of the σ and π states of CH_2.

carbon and nitrogen atoms in the C−N bond of the bent structure. The corresponding trajectories of kinetic and potential energies with respect to the energy of the S_1 Franck−Condon state are shown in Figure 2. From these results, we obtained the upper bound of the activation energy of 0.71 eV, measured from the energy difference between the Franck−Condon transition and the highest potential energy during the dissociation process. Meanwhile, the corresponding activation energy in the ground state, which is obtained with some selected molecular structures, is 2.18 eV. Thus, the activation barrier height in the first excited state was less than half of that in the ground state.

The carbene formation reaction is summarized in the schematic picture in Figure 3. With UV irradiation on diazomethane, one electron is promoted from the n state to the π^* state. The electron promotion corresponds to the Franck−Condon state of the S_1 excited state. In the RTP-TDDFT calculation of the S_1 state, C−N−N stretching followed by mixing with the bending mode occurred, which are represented by (1) and (2) in Figure 3. With the imposed velocity technique, N_2 was extracted, represented by (3).

The final products of the photodissociation are identified as the excited carbene $^1CH_2$ ($^1B_1$) and ground state N_2 molecule by using wave functions analysis, which supports the RIES mechanism. In Figure 4, the red and white spheres represent the isosurfaces with opposite signs of wave function. The HOMO and LUMO levels at the initial time are the well-known n and π^* states of diazomethane. Note that these two levels are both half-occupied by one electron representing the n−π^* S_1 state of diazomethane. During N_2 dissociation, the HOMO and LUMO levels show significant change in the wave function, as shown in Figure 4. Finally, the HOMO and LUMO levels are changed by the σ and π states of CH_2, and the HOMO-1 level changes to the π bonding state of the N_2 molecule. The σ and π states of CH_2 almost degenerated demonstrating the excited carbene formation. The identified carbene state is consistent with recent work which supplies experimental evidence for the direct observation of the excited singlet state of carbene.[24] With a transient peak of ∼20 ps lifetime, they give substantial evidence for the excited singlet state of carbene. As shown in Scheme 2, the excited carbene $^1CH_2$ ($^1B_1$) and ground state N_2 molecule formation are consistent with the RIES mechanism. Since the carbene in this work did not have alkyl radicals, like CH_3, which induce hydrogen migration in the RIES mechanism, successive hydrogen migration from the alkyl radicals is beyond the scope of this paper.

The small activation energy barrier in the first excited states comes from the geometry, in which the HOMO and LUMO levels are very close to each other. This does not correspond to the CI point, but we call this a CI-like structure, since the atomic coordinates are very close to those of the CI points of Yamamoto et al.[12] In previous calculations,[11−13] two CI-like structures, which show the in-plane and out-of-plane bending of N_2 relative to CH_2, were attained with simple diazomethane. Since the in-plane bending CI-like structure gives a small activation energy barrier for carbene formation instead of S_1−S_0 deactivation in previous work, it is expected that a similar activation energy barrier can be found in other out-of-plane bending CI-like structures. We studied the corresponding activation energy barrier of carbene formation from the out-of-plane bending CI-like structure. By doing geometric optimization in the S_1 potential energy surface from a similar molecular structure of another S_1/S_0 CI in their work,[12] we found the corresponding structure. With the imposed velocity technique, the corresponding upper bound of the energy barrier in the S_1 state is estimated at 0.44 eV compared to that of the Franck−Condon initial state. This implies that the route is more probable compared to the previous route if we can reach the out-of-plane bending CI-like structure throughout the RIES dynamics. Another implication of this finding is that further study with distribution over ensemble is needed to obtain the realistic value of the barrier since the photolysis can be available through overcoming activation barrier depending on the process. Our RTP-TDDFT again showed no indication of radiationless transition to the S_0 state consistently with no matching of the HOMO and LUMO levels during the simulation. This fact means that the RTP-TDDFT simulation did not let a trajectory of MD hit the exact CI points. However, the deactivation process through S_1/S_0 CI might also contribute to photolysis if the RTP-TDDFT simulation hits the CI points.

According to recent laser flash experiments, photoexcitations were done with higher energy (λ = 310 nm)[7−9] than red-edge absorption energies (λ = 360 or 345 nm). Thus, it is very likely that photoexcitation with higher energy than the red-edge absorption energy leads to vibronic excited states. If this is true, transition from higher vibrational modes may have kinetic energy relevant to high vibrational energy for overcoming the activation barrier in the electronically excited state. It also is consistent with experimental reports that state that photoreaction is enhanced by shining light in the short wavelength region. The destruction of diazo-precursors of carbene greatly increases and the quantum yield of photodissociation is approximately 10 times larger as the excitation wavelength shortens.[25] This can be explained as enhancement of photoreaction assisted by supplement of kinetic energy from transition to higher vibronic excitation state.

Conclusions

Photolysis of diazomethane has been studied by using RTP-TDDFT calculations. With the Franck−Condon transition limit, the extraction of N_2 and the deactivation from the S_1 to S_0 state through the S_1/S_0 conical intersection did not occur in our calculations, and the electronic state of diazomethane

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remained in the excited state. The upper bound of the activation barrier height in the electronic excited state of diazomethane was estimated by using an imposed-velocity technique and showed a reasonably small quantity of the barrier compared to that under the ground state. As a final product of the photodissociation, the excited state of $^1CH_2$ ($^1B_1$) carbene has been identified, which supports the RIES pathway rather than the S_1/S_0 CI pathway.

Supporting Information Available: The Cartesian coordinates of two CI-like structures for both in-plane and out-of-plane bending geometry and three movies for stretching, bending modes, and the dissociation process. This material is available free of charge via the Internet at http://pubs.acs.org.

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