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REGULAR ARTICLE

Direct ab initio MD study on the hydrogen abstraction reaction of triplet state acetone from methanol molecule

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Abstract Solvent re-orientation process of triplet acetone/methanol complex and intermolecular hydrogen atom abstraction reaction on the triplet state energy surface, $(CH_3)_2C{=}O\ (T_1) + CH_3OH \rightarrow (CH_3)_2C\text{–}OH + CH_2OH$ in gas phase, have been investigated by means of density functional theory (DFT) and direct ab initio molecular dynamics (MD) methods. The static DFT calculation of hydrogen abstraction reaction at the T_1 state showed that the transition state is 16.4 and 30.9 kcal/mol lower than the energy levels of S_1 and S_2 states, respectively, and 9.2 kcal/mol higher than the bottom of T_1 state. The product state, $(CH_3)_2C\text{–}OH\cdots CH_2OH$, is 8.4 kcal/mol lower in energy than the level of T_1 state. The direct ab initio MD calculation showed that the product is rapidly formed within 150 fs and the separated products $(CH_3)_2C\text{–}OH + CH_2OH$ were formed. The mechanism of reaction dynamics of the triplet acetone/methanol complex was discussed on the basis of theoretical results.

Keywords Triplet acetone · Hydrogen abstraction · Ab initio MD · Trajectory

1 Introduction

The reactions of triplet state molecule (via triplet state surface) have been important in biochemistry and photochemistry because the molecules at the triplet state have a highly activity as an intermediate. In particular, the carbonyl compounds have usually a long lifetime, so that several reactions occur via triplet state [1].

For example, Norrish type II reaction is one of the typical reactions of carbonyl compounds at the triplet state (T_1 state) [2, 3]. The C=O carbonyl group abstracts a hydrogen atom of methyl group at the T_1 state (1,5-shift). This reaction occurs efficiently as an intramolecular reaction within the carbonyl compound.

Du et al. [4] measured a nanosecond time-resolved resonance Raman (ns-TR3) spectra of the triplet state benzophenone reaction with the 2-propanol hydrogen-donor solvent. The TR3 spectra show that the benzophenone triplet state ($n\pi^*$) hydrogen abstraction reaction with 2-propanol is very fast (about 10–20 ns) and forms a diphenylketyl radical and an associated 2-propanol radical partner.

From a theoretical point of view, Chen and Fang [5] calculated that potential energy diagram for the Norrish II reaction of butanol using ab initio calculation. The activation energy of the 1,5-hydrogen shift in butanal was calculated to be 27.7 kcal/mol from the bottom of T_1 state.

The structural and electronic properties of the triplet state of acetone in aqueous solution model were studied using an effective QM/MM molecular dynamics (MD) approach [6]. In particular, the striking consequences of the electronic transitions of $n \rightarrow \pi^*$ electron promotion on the acetone structure and on its microsolvation have been analyzed in some detail and compared to the behavior of the acetone ground-state. Moreover, the phosphorescence emission spectrum was calculated on sampled molecular configuration. They showed a Stokes shift in good agreement with available experimental data.

Muldoon et al. [7] showed that the reaction efficiency via triplet state is significantly higher than the S_1 state because the reaction via S_1 state is branched to both

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reactive (1,5-hydrogen shift) and non-reactive (return to the S_0 state) products.

Benzophenone, which is a typical C=O carbonyl compound, reacts with alcohol and causes a hydrogen abstraction reaction. It is known that this reaction occurs efficiently on T_1 state. Acetone, one of the simplest C=O carbonyl compounds, also causes an intermolecular hydrogen abstraction reaction. Nau et al. [8] measured rate constants for quenching of excited state acetone by hydrogen donor tributyltin hydride and 2-propanol using time-resolved spectroscopy. They showed that both singlet and triplet excited states can abstract a hydrogen atom of the donor molecules.

In the present study, an intermolecular hydrogen abstraction reaction of triplet acetone from a methanol molecule in gas phase is investigated by means of density functional theory (DFT) and direct ab initio molecular dynamics (MD) methods [9–11] in order to elucidate the reaction mechanism of triplet C=O carbonyl with a methyl group. Also, the solvent re-orientation process of acetone/methanol 1:1 complex before the hydrogen abstraction was investigated. As a model, a hydrogen abstraction reaction on the T_1 state, $(CH_3)_2C{=}O\ (T_1) + CH_3OH \rightarrow (CH_3)_2C{-}OH + CH_2OH$, was examined in this work.

2 Method of calculation

The geometries of the stationary points of the reaction of triplet acetone with a methanol molecule were fully optimized at the B3LYP/6-311++G(d,p) level of theory [12–14]. The harmonic vibrational frequency of the complex at the optimized point was calculated to elucidate the stability of the complex.

Direct ab initio molecular dynamics (MD) calculation was carried out at the B3LYP/6-311++G(d,p) level of theory throughout. The transition state of hydrogen abstraction reaction was fully optimized by the energy gradient method. The trajectories were run from the transition state geometry. The electronic state of the system was monitored during the simulation. We confirmed carefully that the electronic state is kept during the reaction. The solvent re-orientation process of acetone/methanol system was also investigated with the same manner. A trajectory on the T_1 state was run from the optimized structure of acetone/CH_3OH complex at the S_0 state.

The velocities of atoms at the starting point were assumed to zero (i.e., momentum vector of each atom is zero). The equations of motion for $\boldsymbol{n}$ atoms in a molecule are given by

$$\frac{dQ_j}{dt} = \frac{\partial H}{\partial P_j}$$

$$\frac{dP_j}{dt} = -\frac{\partial H}{\partial Q_j} = -\frac{\partial U}{\partial Q_j},$$

where $j = 1 - 3N$, H is the classical Hamiltonian, Q_j is Cartesian coordinate of the j-th mode and P_j is conjugated momentum. These equations were numerically solved by the Verlet algorithm. No symmetry restriction was applied to the calculation of the energy gradients. The time step size was chosen as 0.10 fs, and a total of 10,000 or 20,000 steps were calculated for each dynamics calculation. The drift of the total energy is confirmed to be less than $10^{-3}\%$ throughout at all steps in the trajectory. The momentum of the center of mass and the angular momentum were assumed to zero. More details of the direct MD calculations are described elsewhere [9–11].

Static ab initio and DFT calculations were carried out using Gaussian 03 program package [15]. To confirm the stability of the molecules at all stationary points, the harmonic vibrational frequencies were calculated at the B3LYP/6-311++G(d,p) level of theory. All vibrational frequencies obtained were positive except for those of TS, indicating that the stationary points were located at the local minima on the potential energy surface. The excitation energies of acetone/CH_3OH complex were calculated by means of time-dependent (TD) DFT method [16, 17]. Ten electronic states were solved. Intrinsic reaction coordinate (IRC) [18–22] of hydrogen abstraction reaction was calculated from the transition state (TS) to both reactant and product directions.

3 Results

3.1 Energy diagram

The energy diagram of the intermolecular hydrogen atom abstraction reaction of triplet state acetone from a methanol molecule is illustrated in Fig. 1. The optimized structures of molecules at the stationary points are illustrated in Fig. 2. The value of energy level is calculated at the B3LYP/6-311++G(d,p) level. At an initial state of the reaction, acetone (Ac) binds to the methanol molecule by a hydrogen bond (S_0 state). By photo-irradiation to the complex, the electronic state is vertically changed to the first and second excited states (S_1 and S_2). In case of acetone, intersystem crossing (ISC) from singlet to triplet states occurs efficiently (quantum yield of ISC is 0.53 ± 0.04) [23–25] and the surface is changed to the T_1 state.

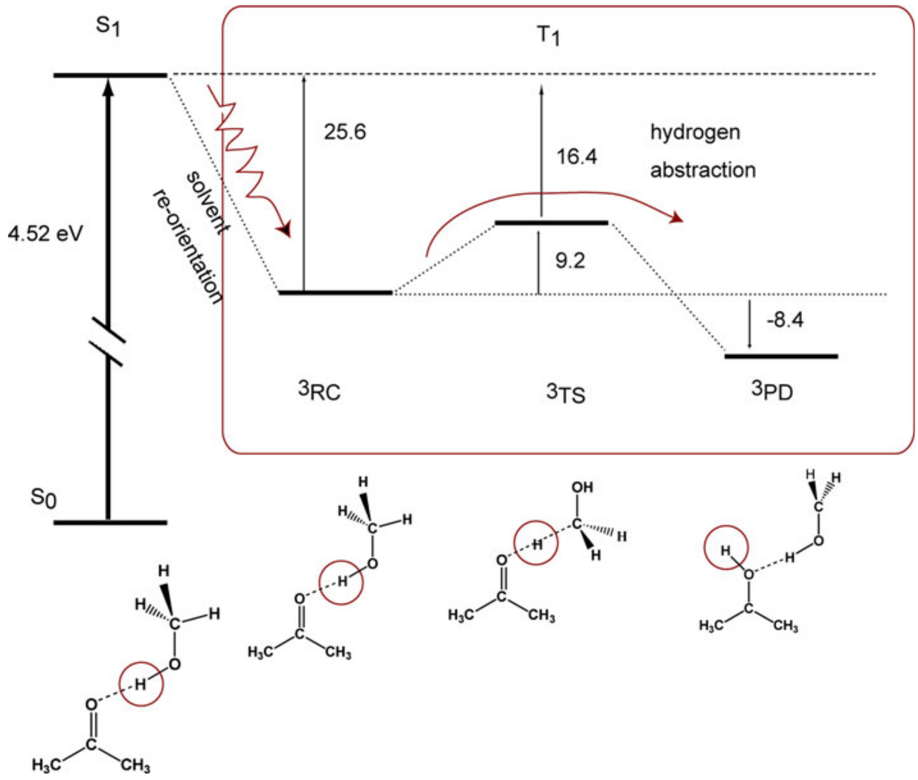

Fig. 1 Energy diagram of hydrogen abstraction reaction of triplet state acetone from CH_3OH. The values were calculated at the B3LYP/6-311++G(d,p) level. ^{3}RC, ^{3}TS and ^{3}PD mean reactant state, transition state, and product state, respectively

The bottom of triplet state (T_1) is 25.6 kcal/mol lower in energy than the vertically excited S_1 state. The point of S_1 state corresponds to the initial state of the hydrogen abstraction reaction on the T_1 state. The energy level of transition state (TS) of the hydrogen atom abstraction reaction is 9.2 kcal/mol higher than the bottom of T_1 state. The product state (PD) is 34.0 kcal/mol lower than the vertically excited S_1 state. Therefore, the hydrogen abstraction reaction is exothermic in the energetics. The energy level calculation suggests that the solvent re-orientation occurs first, and then the hydrogen abstraction proceeds.

3.1.1 S_0 state

Before the photo-irradiation, the complex composed of acetone and methanol molecules is located at the ground state (S_0 state). The optimized geometries at the stationary points along the hydrogen abstraction reaction are given in Fig. 2. The hydrogen atom of CH_3OH orients to the carbonyl oxygen of acetone. The binding energy of CH_3OH to acetone is calculated to be 6.3 kcal/mol. The intermolecular distance between hydrogen of CH_3OH and oxygen of C=O carbonyl (i.e., distance of hydrogen bond) is calculated to be 1.923 Å.

3.1.2 Excited singlet states (S_1 and S_2)

If the complex is photo-irradiated, the electronic state of acetone/CH_3OH (S_0) is vertically excited to the first and second excited states (S_1 and S_2). The energy differences from S_0 to S_1 and S_2 states are calculated to be 4.52 and 5.15 eV, respectively, at the TD-DFT (B3LYP/6-311++G(d,p) level. These states have singlet $n\pi^*$ and $\pi\pi^*$ excited states denoted by $^1(n\pi^*)$ and $^1(\pi\pi^*)$, respectively.

3.1.3 T_1 state

In case of acetone, it is known that the intersystem crossing (ISC) occurs rapidly and the electronic state of acetone/CH_3OH (S_1) is efficiently converted to the T_1 state denoted by $^3(n\pi^*)$.

The intermolecular distance r(CO–HO) of acetone/CH_3OH (T_1) is calculated to be 2.027 Å, which is slightly longer than that of the singlet ground state (1.923 Å). The energy level of $^3(n\pi^*)$ triplet state is 25.6 kcal/mol lower than that of the S_1 state.

3.1.4 Transition state (TS) and product state (PD)

Transition state structure of the complex was fully optimized by means of energy gradient method. In the optimized structure, the distances of transferred hydrogen atom from carbonyl oxygen and methyl carbon are $R_1 = 1.336$ Å and $R_2 = 1.236$ Å, respectively. The oxygen–carbon distance is 2.572 Å, which is significantly shorter than that of S_0 state. The activation energy of TS relative to T_1 state is calculated to be 9.2 kcal/mol. The excess energies of TS are

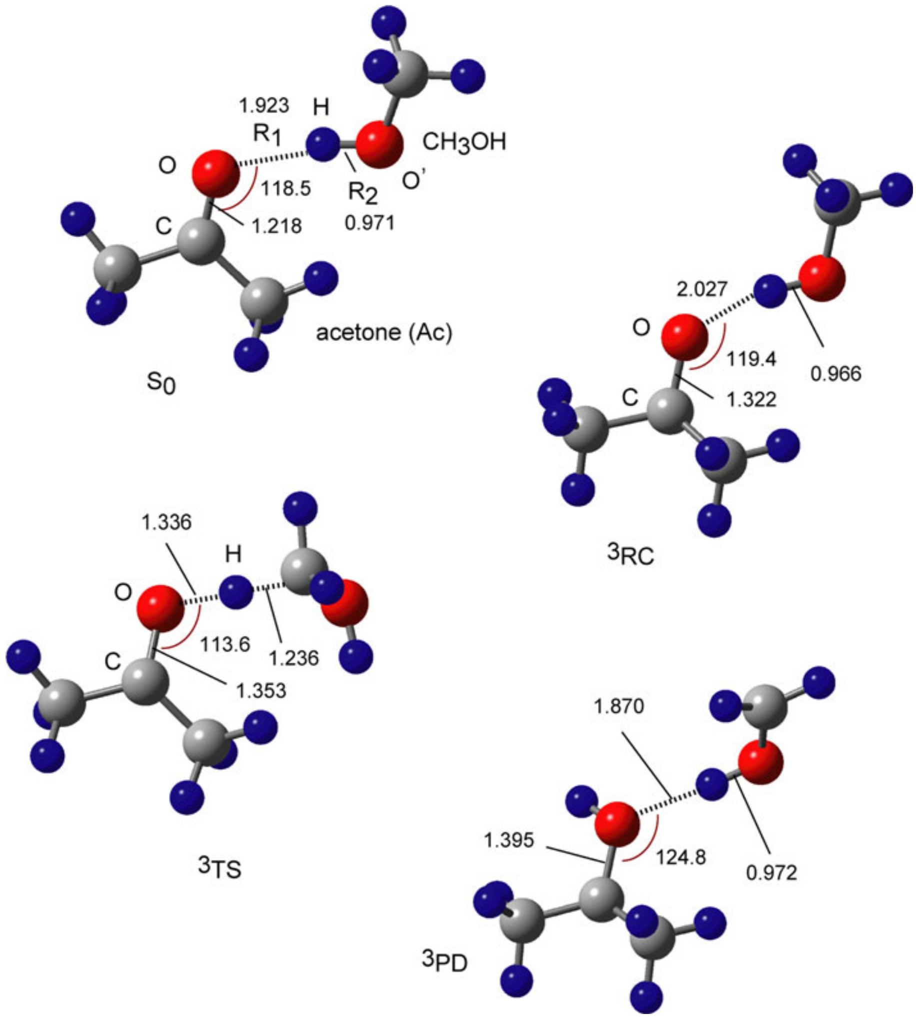

Fig. 2 Optimized structures and geometrical parameters of ^{3}RC, ^{3}TS and ^{3}PD. Distances are in Å

16.4 kcal/mol (vertical excitation to S_1 state) and 30.9 kcal/mol (S_2 state). Imaginary frequency of TS is calculated to be 1,087i cm^{-1}. From analysis of vibrational mode, it is assigned that the imaginary frequency of TS is asymmetric stretching mode composed of ($HOCH_2 \cdots H \cdots O{=}C$).

The energy level of product state (^{3}PD) is −8.4 kcal/mol relative to the T_1 state. The distance between CH_2OH radical and hydroxyl alcohol radical $C(CH_3)_2OH$ is 1.870 Å.

3.2 Zero-point energy dynamics on S_0 state

In an actual complex, the structure fluctuates because of zero-point vibration (ZPV). The results of direct ab initio MD calculations of the complex with zero-point energy (ZPE) on the ground state S_0 state are illustrated in Fig. 3. The ZPE dynamics calculation showed that the potential energy oscillates periodically as a function of time, and the structural conformation of the complex changes markedly over time during the simulation. However, the hydrogen bond is retained during the simulation.

3.3 Solvent re-orientation dynamics on the T_1 surface

First, the solvent re-orientation of CH_3OH around the triplet acetone (T_1) may occur before the hydrogen abstraction of triplet acetone. In this section, the solvent re-orientation process in gas phase was investigated by means of direct ab initio MD method. Potential energy of the system is plotted as a function of time in Fig. 4. The structure at time zero was assumed to that of S_0 state. After the excitation to the T_1 state, the energy decreases gradually with a vibrational structure. The intermolecular distance r(H–O) is elongated from 1.922 Å (time = 0.0 fs) to 2.163 Å (121 fs). This bond elongated is caused by a spontaneous weakening of the hydrogen bond after the S_0–T_1 transition. Also, it was found that the planar structure around a C=O carbonyl of acetone is changed to a bent form. The position of methanol was changed from ***n***-orbital of the carbonyl to π-orbital orientations.

The energy of the system was stabilized to −10.5 kcal/mol after the solvent re-orientation. The time profile of energy vibrates periodically and the solvation

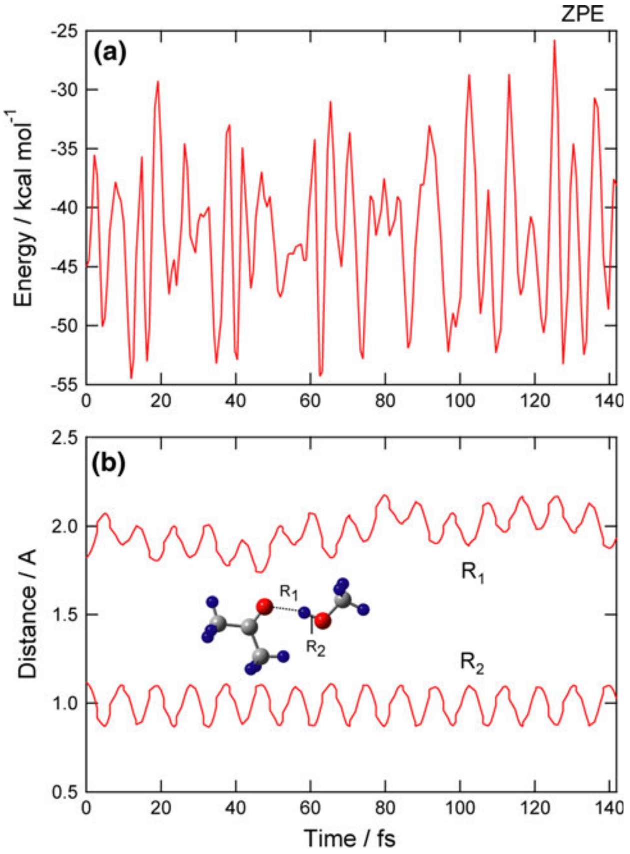

Fig. 3 Potential energy (*A*) and atomic distances (R_1 and R_2 in Å) of acetone/methanol complex with zero-point energy plotted as a function of time, obtained by means of direct ab initio MD calculation at the B3LYP/6-311++G(d,p) level

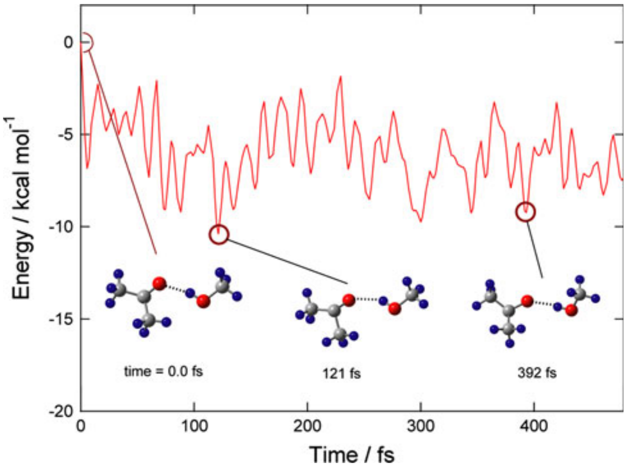

Fig. 4 Time profile of potential energy of acetone/methanol system following excitation to the triplet state surface obtained direct ab initio MD calculation at the B3LYP/6-311++G(d,p) level. Inserted structures show snapshots of acetone (T_1)/methanol complex after the triplet state excitation

structure is gradually changed as a function of time. Thus, the solvent re-orientation takes place spontaneously after the T_1 state.

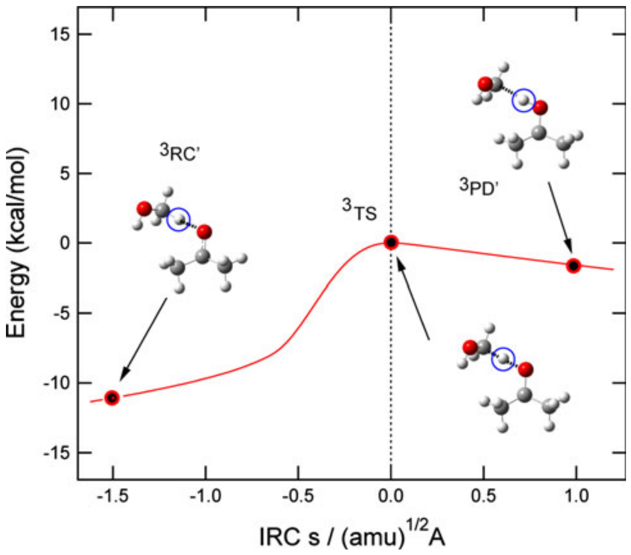

Fig. 5 Intrinsic reaction coordinate (IRC) for the hydrogen abstraction reaction of triplet state acetone from CH_3OH

3.4 Intrinsic reaction coordinates (IRC)

In the IRC calculation, the first, the transition state of hydrogen abstraction reaction is obtained at the B3LYP/6-311++G(d,p) level. The optimized geometry was illustrated in Fig. 2 (^{3}TS). This structure has an imaginary frequency (1,087 cm^{-1}). The IRC was calculated using normal mode corresponding to the imaginary frequency for the forward and backward directions.

The IRC is plotted in Fig. 5 as a function of reaction coordinate (***s***). The structures of reactant intermediate (^{3}RC’), transition state (^{3}TS) and product intermediate (^{3}PD’) calculated along the IRC are illustrated as insert figures. At ^{3}RC’ ($\boldsymbol{s} = -1.5$), the distances R_1 and R_2 are 1.690 and 0.969 Å, respectively. The structure of ^{3}PD’ ($\boldsymbol{s} = +1.0$), the distances R_1 and R_2 are 0.984 and 1.609 Å, respectively.

In order to confirm the true transition state connecting between RC and PD states, the geometry optimizations were carried out from the intermediates (^{3}RC’ and ^{3}PD’) in the IRC. The geometry optimizations from ^{3}RC’ and ^{3}PD’ gave ^{3}RC and ^{3}PD, respectively. The results indicate that the transition state (TS) is actually connected between reactant (^{3}RC) and product (^{3}PD) states in the hydrogen abstraction reaction.

3.5 Reaction dynamics from transition state (TS)

To elucidate the reaction dynamics of intermolecular hydrogen abstraction of triplet acetone molecule from CH_3OH, direct ab initio MD calculation was carried out at the B3LYP/6-311++G(d,p) level. The calculations were

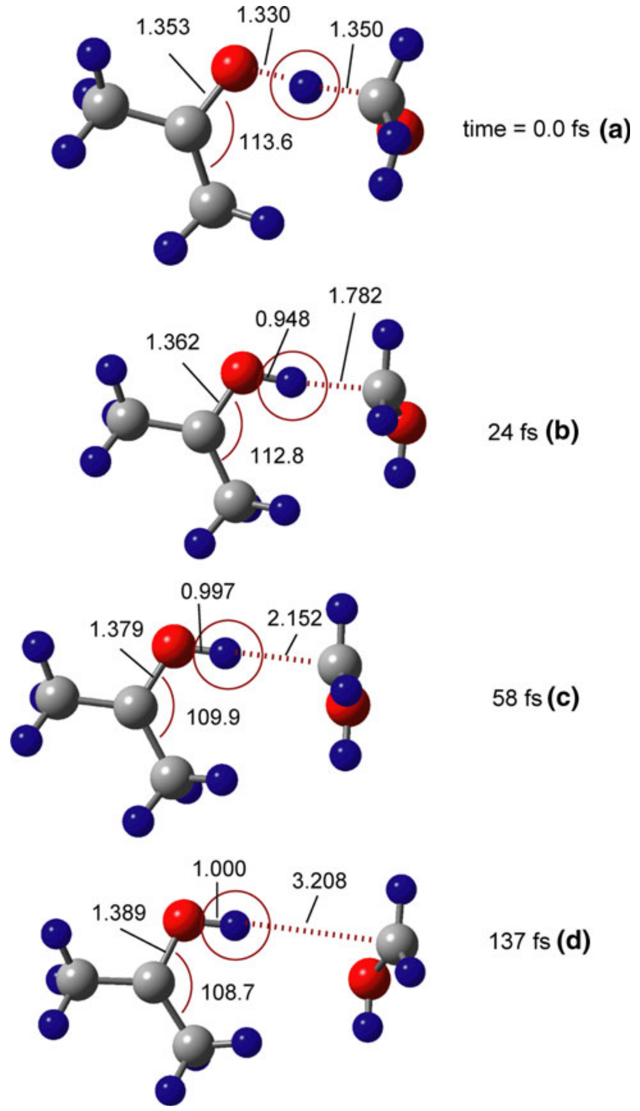

Fig. 6 Snapshots of hydrogen abstraction reaction of triplet state acetone from CH_3OH obtained direct ab initio MD calculation at the B3LYP/6-311++G(d,p) level

started from around TS structure to forward (PD) and backward (RC) directions (Fig. 6).

Snapshots and potential energy as a function of time are illustrated in Fig. 7. At time zero, the structure is close to that of TS. After the starting the reaction, O–H distance of $C(CH_3)_2OH$ radical is rapidly shortened (R_1), indicating that the hydrogen of the O–H group of methanol is abstracted by the carbonyl oxygen C=O. For example, the O–H distances at time = 0 and 24 fs are 1.330 and 0.948 Å, respectively. In addition, the product of CH_2OH radical is gradually leaved from a protonated acetone. The distances of O–C (acetone oxygen and methyl carbon) are 2.648 Å (time = 0.0 fs), 2.727 Å (24 fs), 3.126 Å (58 fs) and 4.197 Å (137 fs).

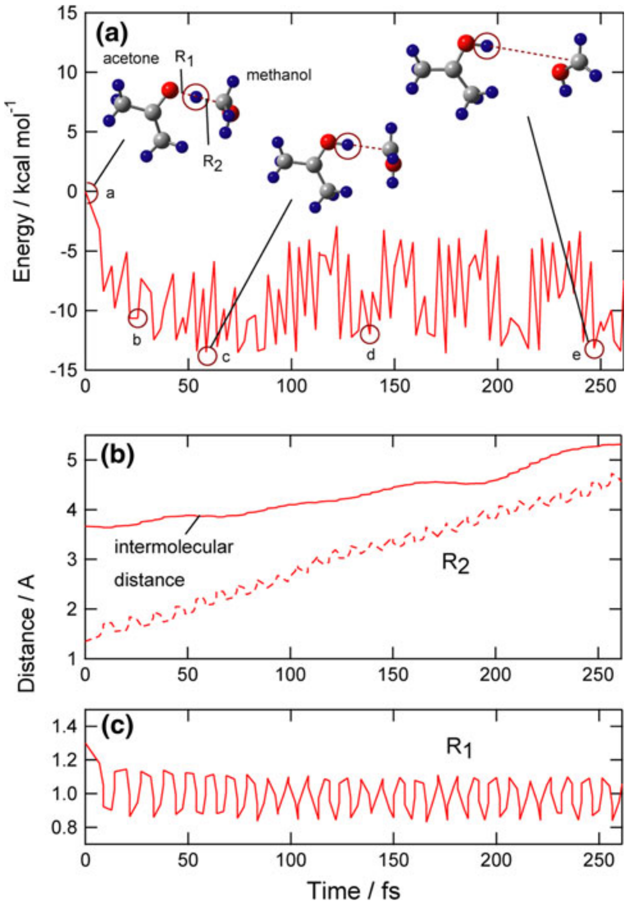

Fig. 7 Time profiles of potential energy and atomic distances of acetone/methanol system. The trajectory was started from near TS of the hydrogen abstraction reaction

The potential energy (PE) and bond distances of the system are plotted in Fig. 7 as a function of time. The PE goes down rapidly within 50 fs, and is minimized at 58 fs. (point **c**). The lifetime of ^{3}TS is roughly estimated by 90 fs in this trajectory. A complex with a large amplitude mode between OH and alcohol radical is formed as a product. Finally, separated products were formed.

3.6 Effects of initial structures of the complex at the TS on the dynamics

In the previous section, only one trajectory was discussed as a representative case. In this section, several trajectories initiated at different geometries around TS are compared. A total of ten trajectories were run. The time profiles of potential energies of four trajectories are plotted in Fig. 8. All trajectories exhibited the similar energy changes in the reactions. The general results were thus not dependent on the initial structure of TS.

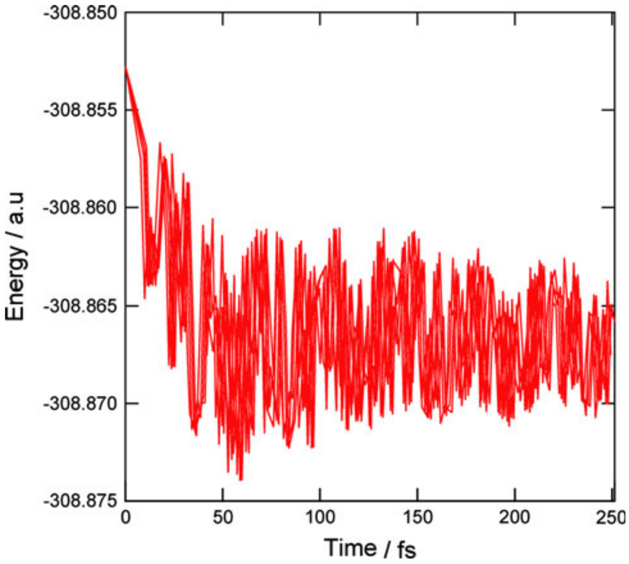

Fig. 8 Effects of initial conditions for the trajectories on the hydrogen abstraction dynamics of the acetone (T_1)/methanol system. The plot shows the time-dependence of potential energy. Four trajectories from different selected initial structures are shown

4 Summary

In the present study, first, the solvent re-orientation of methanol molecule around acetone by the photo-irradiation to the triplet state was investigated by means of direct ab initio MD method. Next, a hydrogen abstraction reaction of acetone from methanol molecule was investigated. The transition state is 9.2 kcal/mol lower than that of S_1 state, and the product state, $(CH_3)_2C$–OH···OH, is 8.4 kcal/mol lower in energy than that of T_1 state. The direct DFT-MD calculation showed that the product is rapidly formed within 50 fs and the separated products $(CH_3)_2C$–OH + CH_2OH are formed.

We considered only triplet state potential energy surface throughout. Recently, the reaction via singlet excited S_1 state has been also observed experimentally. Nau et al. [8] showed that the S_1 acetone has a higher reactivity but lower efficiency than the reaction via T_1 state. This is attributed to an efficient radiationless deactivation on the S_1 state.

To elucidate the overall reaction, in addition to the reaction on the T_1 state, reaction dynamics on the S_1 and S_2 states are also needed. However, it is known that the reaction efficiency (quantum yield) is significantly reduced by addition of the triplet quencher [26]. Hence, the T_1 state is correlated strongly to the reaction mechanism. The present work provided one of the theoretical aspects about the reaction dynamics of C=O carbonyl.

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