Unveiling electron momentum spectroscopy of Acetone upon 195nm laser excitation by nonadiabatic ab initio molecular dynamics simulation

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[Abstract] The photodissociation of deuterated acetone upon 195nm laser excitation were investigated by employing the trajectory-based on-the-fly nonadiabatic *ab initio* molecular dynamics (AIMD) simulations with the potential energies and gradients calculated at CASSCF/6-31+G** level. The primary methyl radical dissociation take place in S_2 state and yields to the linear 3s acetyl radical. When the C-C bond length increase to ~3.0 Å, the 3s acetyl radical splits into two distinct pathways, immediate cascade $S_2 \rightarrow S_1 \rightarrow S_0$ hopping within 100 fs or stay in the 3s Rydberg state for a certain time (0.3-6.0 ps) before that. The secondary methyl dissociation occur in the ground state of acetyl radical, and due to the rather high kinetic energies, the ground state lifetime is short. The dynamical properties of deuterated acetone, such as lifetimes of intermediates, correlation between vibration modes and competition between different reaction pathways were analyzed.

[Introduction] Acetone photodissociation is a classical prototype of the α-CC bond cleavage reaction, which plays fundamental importance in understanding the dynamics of the entire class of carbonyl compounds. [1] Although the photodissociation dynamics of acetone upon 195nm laser excitation ($S_0 \rightarrow S_2$) have been extensively studied, debates among three mechanisms still exists. [2] The first commonly adopted one is "T_1 dissociation mechanism". The S_2 population decay to the T_1 state via fast internal conversion and intersystem crossing, then the primary dissociation take place by overcoming a low barrier and yield to the ground state acetyl radical. Later, the linear acetyl radical was observed in its first excited state, $CH_3CO(\tilde{A})$, which relates to a much lower dissociation barrier compare with those leading to the bent form $CH_3CO(\tilde{A})$. This result supports that the direct dissociation in S_1 state may be more favorable than the ISC to T_1 state, and the mechanism is namely as "S_1 dissociation mechanism". Similar process can also take place in S_2 state with a barrier of ~0.7 eV, then the linear 3s acetyl radical, $CH_3CO(3s)$ could arrive the $S_2/S_1/S_0$ conical intersection along the basically barrierless potential energy surface. This "S_2 dissociation mechanism" was further confirmed by high level *ab initio* calculations. [3] In this study, the on-the-fly trajectory surface hopping dynamic simulations were performed to detecting the acetone dissociation mechanisms started at S_2 state and the preliminary results are presented.

[Methods] The on-the-fly trajectories are propagated by numerically integrating the Newtonian equation of motion on the basis of the velocity-Verlet method with potential energies and the corresponding analytical gradients calculated at CASSCF/6-31+G** level by employing the MOLPRO program. [4] As the primary reaction coordinate is a high frequency C-C stretching mode, the time step for the trajectory simulation is set as 0.2 fs. Along the trajectory propagation, the improved Zhu-Nakamura formulas [5,6] were utilized to calculate the global nonadiabatic switching probability at the avoided crossing points, which were detected by locating minimum separation between two adjacent adiabatic potential energy surfaces in three consecutive time steps. The surface hopping detection along trajectory is activated when the potential energy gap is smaller than 0.5 eV. For the detail description of this surface hopping method, please see ref.5.

[Results and Discussion]

Within the simulated trajectories, the primary α-CC cleavage take place prior to the S_2/S_1 surface hopping, which agree with the "S_2 dissociation mechanism". The direct dissociation precedes via joint contribution of OCC bending and C-C stretching modes. Accompanied with C-C bond breaking, the acetyl part become linear and the methyl radical lie in the perpendicular direction to the central carbon atom. As shown in Fig. 1, the S_2/S_1 hops can be classified into two categories with CC bond lengths of ~1.5 (A) or ~1.9 Å (B). For the latter case, the CO bond may be triple or double and which distributed in wider region up to 1.3 Å. For the consecutive S_1/S_0 hop, the CC bond length of category A ones stay in similar region but the CO length evidently increased. For category B, the CC bond distribution move to smaller region, however the CO region slightly increased. The OCC bending and HHHC umbrella motion were enhanced at S_1/S_0 hops, which is due to the larger kinetic energies that conversed from potential energies. In between the acetone primary α-CC breaking and S_2/S_1 surface hopping, the lifetime of 3s acetyl radical span in a very wide region. About 40% of acetyl radicals stay in 3s state for less than 0.1 ps and the rest ones possess much longer lifetimes up to 6.0 ps. The entire decay procedure of 3s acetyl radical to ground state is ultrafast with a time constant of sub 0.1 ps. The secondary methyl dissociation occur in the acetyl radical ground state, where the equilibrium OCC moiety is highly bent and the methyl radical leaves in semi perpendicular direction to the CO. Due to the high excitation energy of 195 nm laser, the ground state acetyl radical possesses rather large kinetic energy, which will result in short lifetime.
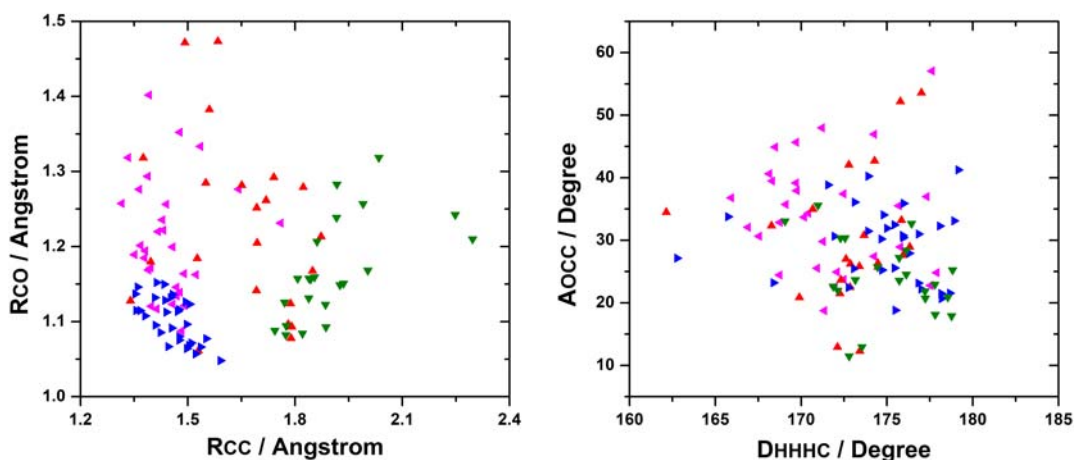

Fig. 1. Selected internal coordinates for conical intersections. Category A and B S_2/S_1 hops are in blue and green, respectively, and the corresponding consecutive S_1/S_0 hops are in cyan and red.

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