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Photodissociation dynamics of propyne at 193 nm: A trajectory surface hopping study

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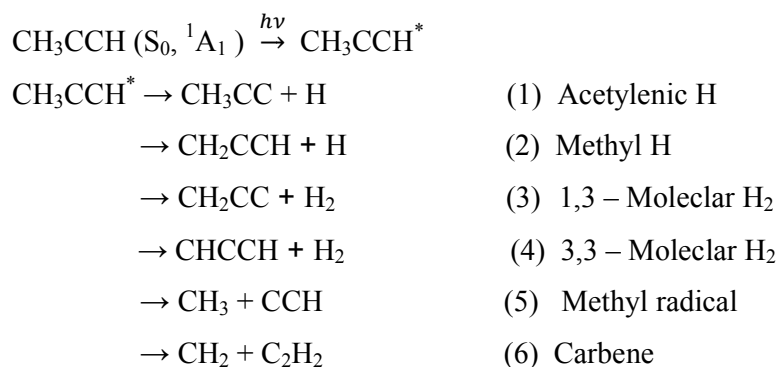
Photodissociation dynamics of propyne at 193 nm is studied using the fewest switches nonadiabatic trajectory surface hopping method on its first excited singlet electronic state ($1^1A''$). The trajectories are propagated based on potential energies, gradients and nonadiabatic couplings calculated at MRCIS (6,7) level with 6-31++G(d,p) basis set. Our trajectory calculations have revealed that $H + H_3CCC$ is the major dissociation channel which has also been predicted, experimentally. For the primary photodissociation channel $H + H_3CCC$ we demonstrate that nonadiabatic dynamics does not play any significant role. This observation is however contradictory to most of the previously reported experimental predictions. Calculated product translation energy distribution for acetylenic H atom elimination peaked at ~ 18 kcal/mol indicates that the dissociation occurs adiabatically on a moderately repulsive excited surface that correlates with the ground state products ($CH_3C\equiv C + H$). H atom elimination process from the methyl fragment involving a transition state, has to compete with acetylenic H atom dissociation channel with no barrier in the excited singlet surface, was found to be too less probable to have contribution to the product branching. We observed less but significant number of trajectories led to the $CH_3 + CCH$ products formation which has not been observed experimentally when propyne is excited at 193 nm.

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I. Introduction

A comprehensive knowledge of the photodissociation dynamics of propyne is of great importance as it plays a crucial role in atmospheric¹, interstellar², and combustion chemistry.^{3, 4} Specifically, observation of warm molecular clouds from propyne,⁵ formation of benzene and hence polycyclic aromatic hydrocarbons (which are undesirable pollutants) in flames by chemically activated addition and isomerization of 1,3-butadienyl and acetylene,³ etc, are few known examples.

Photodissociation of propyne has been studied experimentally at various wavelengths.^{1, 6-16} From these studies one can propose the following channels for the photodissociation of propyne:



When the ground state propyne ($S_0, {}^1A_1$) is photoexcited it goes to excited electronic state. The excited propyne can undergo H atom fragmentation either from acetylenic group leading to channel (1) or from the methyl fragment resulting into channel (2). This H atom fragmentation can take place adiabatically on the excited state or can happen in the ground electronic state after nonadiabatic transition from the excited state. There is a possibility of molecular H₂ elimination from the excited propyne, which can be either 1,3-elimination i.e. channel (3) or 3,3-elimination from the methyl fragment leading to channel (4). The fragmentation of the excited propyne may take

place through C – C bond cleavage producing methyl radical, i.e. channel (5). If H atom migration takes place from methyl fragment to the middle carbon of the propyne followed by C-C bond breaking we get carbene and acetylene resulting to channel (6).

Seki and Okabe⁷ using Fourier transform infrared spectroscopy concluded that despite methyl C-H bond being weaker compared to acetyl C-H bond, only acetylenic H atoms were found with no evidence for the dissociation of methyl H when propyne was excited at 193 nm. Satyapal and Bersohn¹¹ observed exclusively D atoms from the photodissociation of $\text{CH}_3\text{C}_2\text{D}$ at 193 nm, with no trace of H atoms. This observation indicates that dissociation is faster than internal vibrational energy redistribution. Later, Jackson and co-workers¹⁴ used vacuum ultraviolet (VUV) laser photoionization in combination with time-of-flight (TOF) mass spectrometry to determine the photofragments produced from the laser photodissociation of propyne in a molecular beam and came to the same conclusion. Almost simultaneously, Sun *et al.*¹⁶ have investigated the photodissociation of propyne at 193 nm using a molecular beam with electron impact ionization and tunable VUV light to photoionize the photoproducts and reiterated that channel (1) i.e., the propynyl (H_3CCC) radical is the major H atom dissociation channel, not channel (2) in which H atom dissociation takes place with the formation of propargyl (H_2CCCH) radical.

Qadiri *et al.*¹ have reported time-of-flight (TOF) measurements of the H (and D) atoms resulting from photolysis of jet-cooled CH_3CCH and $^{13}\text{CD}_3\text{CCH}$ molecules at 193.3 nm and proposed that H atom elimination occurs through channel (2). The photofragmentation dynamics has been studied by H(D) Rydberg atom photofragment translational spectroscopy (PTS). Their PTS study indicated that fragmentation is

preceded by internal conversion (IC) isomerization to allene, on the ground state potential energy surface (PES). More recently, PTS study of the dissociation dynamics of propyne at 193 nm by Neumark and co-workers¹⁷ also predicted that the H atom loss mostly occurs from the methyl group and proceeds largely statistically, after IC onto the ground electronic state PES. This observation however contradicted their previous study¹⁶ of the same group and also other experimental studies reported earlier,^{11, 12, 14} in which it was concluded that acetylenic H is the major source of H atom dissociation channel with no trace of methyl H atoms.

Photodissociation dynamics is predicted to be different when propyne is excited at lower wavelengths. Harich *et al.*¹⁵ investigated photodissociation dynamics of propyne at 157 nm using PTS. This study clearly demonstrates that H atom elimination occurs from both the methyl (CH₃) and acetyl (C≡C-H) groups. They also observed that the H atom elimination from the methyl group is a single dynamical process while acetylenic H elimination shows two distinctive dynamical pathways; the former is faster and the later one is slower with a ratio of 0.30:0.43. A similar conclusion was made by Qadiri *et al.*¹ from the observed TOF spectra of the H and D atoms resulting from the photolysis of CH₃CCH and ¹³CD₃CCH when excited at 121.6 nm. The slower dissociation process involves IC into a lower electronic state, isomerization and subsequent unimolecular decay. On the other hand, selective cleavage of the acetylenic C-H bond which presumably occurs in the excited electronic state after photoexcitation of propyne appears to be the fast dissociation decay.

Mebel and co-workers¹⁸ have carried out extensive *ab initio* calculations to investigate the photodissociation dynamics of propyne. Their calculations suggested that the photodissociation of propyne at 193 nm occurs through a Frank-Condon transition to the excited state 1E followed by IC into the vibrationally excited ground electronic state, and then there is a possibility that propyne can either dissociate to $HCCH + H_2$ or isomerizes to allene which eventually undergoes the H_2 elimination giving H_2CCC . They however, proposed that the H_2 elimination is a minor channel of propyne photodissociation, while elimination of the acetylenic H atom is the major channel. In addition, they showed that the vertical excitation to the 1E state involves excitation of the normal modes corresponding to the CCC and CCH bending and C-H stretching of the acetylenic hydrogen, while the methyl fragment remains unaffected. This prediction was supported by some of the experimental observations that the elimination of the acetylenic (but not methyl) hydrogen is the major photodissociation channel of propyne at 193 nm, even though the methyl C-H bond is much weaker, comparatively. Cui *et al.*¹⁹ studied the photodissociation of acetylene from S_1 and suggested that when excitation is done at 193 nm a nonadiabatic photodissociation channel is preferred which involves a $S_1 \rightarrow S_2$ transition followed by a $S_2 \rightarrow S_0$ surface crossing producing mainly C_2H ($X^2\Sigma^+$). Purely based on the similarity of the excited state surfaces of propyne and acetylene, Mebel *et al.*¹⁸ proposed that the fast dissociation of the acetylenic H proceeds via a nonadiabatic path along the S_1 and S_2 surfaces followed by the $S_2 \rightarrow S_0$ and elimination of the H atom giving H_3CCC . A slower and less probable dissociation occurs via IC into the internally excited ground electronic state and a redistribution of the energy between vibrational degrees of freedom. Propyne, then can eliminate either a methyl H or H_2 on the vibrationally excited ground electronic state. One should note that this study is mainly confined to

quantum chemical calculations of the stationary points and energetics along the dissociation pathways. Jackson and coworkers^{13, 14} also proposed that the photodissociation of propyne takes place in the ground electronic state after IC from the excited state (S_1) to the ground state (S_0) and the contribution is estimated to be ~10%. They have, however, predicted that IC of the electronically excited propyne to the ground state surface should compete with direct dissociation on the excited state.

Clearly the controversy exists among the experimental studies regarding the photodissociation dynamics of propyne at 193 nm. To have a complete understanding and quantitative determination of the mechanism of the photodissociation dynamics of propyne one has to perform a high-quality dynamics calculations over the full range of configurations on the surface explored during the dissociation process. This is because only stationary points on the potential energy surfaces are not enough evidence for proposing the actual photodissociation mechanism. Therefore, in the present study we have carried out a nonadiabatic trajectory surface hopping (TSH) dynamics to investigate the photodissociation dynamics of propyne when excited at 193 nm aiming to resolve the controversy among different experimental findings. In this paper, we present the results of direct dynamics study of the photodissociation dynamics of propyne starting from its lowest excited singlet (S_1) state using MRCIS potential energy surfaces, gradients and coupling coefficients.

Performing coupled-state quantum dynamics calculations to study the photodissociation of propyne is highly prohibitive due to involvement of large number of degrees of freedom and multiple coupled electronic states. Instead, we have used Tully's fewest switches trajectory surface-hopping (FS-TSH) method^{20, 21}

which is easily adaptable to any molecule and any number of coupled potential energy surfaces with available nonadiabatic couplings. Of course the method will be efficient provided the dynamics takes place rapidly enough that both the trajectories and time-dependent Schrödinger equation for the electronic state populations can easily be integrated. The NEWTON-X²² molecular dynamics code in conjunction with COLUMBUS²³ electronic structure package allows us to perform nonadiabatic trajectory surface hopping (TSH) calculation on-the-fly with the MRCIS method. Propyne in the first excited state (S_1) dissociates on the femtosecond time scale. Therefore, as long as FS-TSH describes accurate nonadiabatic dynamics, this approach will provide a meaningful picture of the photodissociation mechanism of propyne which has, so far, not been explored.

II. Electronic structure of propyne

The vertical excitation energies were calculated for propyne in its equilibrium geometry using multireference methods such as MRCIS and MRCISD^{24, 25} with various active spaces using the 6-31++G(d,p) basis set.^{26, 27} The equilibrium geometry of propyne refers to an optimized geometry at the B3LYP/6-31++G(d,p) level as implemented in Gaussian 09 package,²⁸ with no symmetry restriction. For comparison the main geometrical parameters obtained at multireference methods (MRCIS, MRCISD) using the 6-31++G(d,p) basis set are also tabulated in Table 1 along with the data obtained at the B3LYP/6-31++G(d,p) level of theory. We find that all the three methods generate almost identical geometrical parameters for the equilibrium geometry of propyne. Subsequent use of the multireferenced methods (MRCIS, MRCISD) for computing the vertical excitation energies are based on a three-state (S_0 , S_1 and S_2) state averaged calculation and a (6E,7O) active space as depicted in

Fig. 1. The active space consists of two π, π^* pair in the acetylene group, a σ^* orbital centered on methyl CH bonds, a diffused 3s Rydberg orbital on carbon of the methyl group and a σ^* orbital mainly confined to acetylenic CH. These calculations were performed using COLUMBUS program.²³ There are three low energy singlet excited states of propyne with symmetries 1E , 1A_2 , and 2^1A_1 within C_{3v} symmetry group which are of $\pi \rightarrow \pi^*$ type. It is worth noting that the lowest singlet excited state 1E of C_{3v} symmetry splits into $2^1A'$ and $1^1A''$ components when symmetry is reduced from C_{3v} to C_s , both with cis and trans geometries.¹⁸ For the first three singlet excited states vertical excitation energies are summarized in Table 2. Corresponding oscillator strengths are also incorporated in the table using square brackets.

We find that the lowest singlet excited state 1E lies 6.78 eV above the ground state using MRCIS(6,7) method. This vertical energy value is calculated to be of 6.72, 6.73 and 6.79 eV when we increase the size of the active space to (8,8), (8,9) and (8,10), respectively. Experimental spectrum⁶ shows that this excitation energy is about 7.19 eV. From Table 2 it is clear that increase in size of the active space (6,7) does not really improve the deviation of the vertical excitation energy. However, MRCISD(6,7) method yields a vertical excitation energy of 7.09 eV, close to the experimental value of 7.19 eV. The vertical energy values calculated using CASSCF(6,7) method is also included in Table 2 to assess the dynamic correlation effect. Calculated electronic oscillator strengths for the first three transitions to states $1^1A'$, $2^1A'$, and $1^1A''$ differ significantly with the size of the active spaces chosen (6,7), (8,8), (8,9) and (8,10), in our calculations. One should however, note that the calculated electronic oscillator strengths using MRCIS(6,7) and MRCISD(6,7) methods are very close.

Figure 2 shows a potential energy diagram for two singlet states S_0 ($^1A'$) and S_1 ($^1A''$) of propyne which are correlated to the lowest states of different product fragmentations $H + C_3H_3$ (Fig. 2(a)), $H_2 + C_3H_2$ (Fig. 2(b)) and, $CH_3 + CCH$ and $CH_2 + HCCH$ (Fig. 2(c)). The energy values calculated at the MRCIS(6,7)/6-31++G(d,p) level are reported in curly brackets. For comparison the energy values calculated at the MRCISD(6,7)/6-31++G(d,p) level are incorporated in square brackets. In general, the energy values for the stationary points are very comparable in both the MRCIS and MRCISD methods, except for the transition states. The transition state energy values computed using MRCIS method are less up to ~ 20 kcal/mol when compared to MRCISD method. All the stationary point calculations were performed using MOLPRO suite of program²⁹ using numerical gradients and with no symmetry constraints.

The H atom gets eliminated from the acetylenic group (channel (1)) following an adiabatic path on the S_1 state and the possibility of a nonadiabatic path to end up on the ground state (S_0) through the $S_1 - S_0$ transition is very unlikely. By inspecting the topology of the surfaces we understand that the nonadiabatic path is unlikely to be followed presumably because of very low transition probability between S_1 and S_0 due to high energy gap before dissociation starts and in fact none of the trajectories followed this path which we will discuss in section III(B). Mebel *et al.*¹⁸ proposed, following the work of Morokuma and co-workers,¹⁹ that the elimination of acetylenic H occurs starting on the S_1 surface and then hops to the S_2 surface followed by the $S_2 \rightarrow S_0$ crossing. C–H bond dissociation energy of methyl group (channel (2)) is lower than acetylenic C–H bond. This channel in the excited state PES however, involves a transition state, TS1, which is at ~ 134 kcal/mol (using MRCIS method) or

~ 141 kcal/mol (using MRCISD method) higher in energy compared to the ground state. Therefore, H atom dissociation through channel (2) is less probable to be followed dynamically as this channel has to compete with channel (1) in the excited PES with no barrier to the dissociation reaction.

From Fig. 2(b) it is clear that the H₂ elimination channels (channels 3 and 4) in the first excited state S₁ are not energetically favourable because of high (at least comparable to or higher than 193 nm with respect to the ground state) energy barriers (associated with TS3 and TS4) to the H₂ elimination reaction. We observed that none of the trajectories completed in the H₂ elimination channels.

C-C bond rupture pathways are shown in Fig. 2(c). Our calculations at the MRCIS(6,7) level indicate that channel (5), involving C-C bond cleavage (possesses no barrier in the S₁ state) forming CH₃ and CCH fragments, is energetically feasible in the excited S₁ electronic state with excitation energy of 193 nm. Channel (6) which forms CH₂ and C₂H₂ after C – C bond breaking (through TS7) preceded by H atom migration from methyl group to the middle carbon atom is also energetically feasible at the same excitation energy but dynamically has to compete with channel (5).

We have computed absorption spectrum of propyne using the nuclear ensemble approach³⁰ as implemented in NEWTON-X program.²² We used 808 single point calculations at the three-state (1 ¹A', 2 ¹A', 1 ¹A'') state-averaged (1:1:1) MRCIS (6,7)/6-31++G(d,p) level of theory to simulate the spectrum. The geometries for these calculations were sampled applying Wigner distribution function, using computed frequencies of the normal vibrational modes in the ground electronic state.

The normal mode frequencies were computed at the UB3LYP/6-31++G(d,p) level of theory using Gaussian 09 suite of program.²⁸ The oscillator strength is calculated for each geometry. The transitions are then accepted based on the ratio of actual value of the transition probability to that at its maximum, with no energy restrictions. The overall absorption peak is the weighted sum of all these accepted individual Gaussians. The resulted absorption spectrum is shown in Fig. 3 along with the measured absorption cross sections of propyne in the 190-230 nm region taken from the work of Fahr and Nayak.⁶ The simulated absorption spectrum including excitation to S_1 and S_2 states is very comparable to the experimental one and has a peak at ~ 181 nm. The experimental spectrum is a broad continuum with a maximum at 172.4 nm overlapped by two additional diffused bands. The redshift of the calculated absorption spectrum is due to error in the MRCIS calculations which is consistent with underestimation of the vertical excitation energy calculation by MRCIS as can be seen from Table 2. It is worth pointing out here that the diffused shoulder in the experimental spectrum is due to transition to a dissociative continuum.³¹ Our computations of absorption spectra with larger active spaces indicate that intensity decreases significantly with inclusion of more number of active electrons. The calculated maximum intensity value using a (8E,8O) active space is very close to the experiment.

III. TSH Calculations

A. Details of calculations

Photodissociation dynamics of propyne in the first excited state is studied using Tully's 'fewest switches' trajectory surface hopping (TSH) method^{20, 21} as implemented in NEWTON-X²² molecular dynamics code. This code is combined with

COLUMBUS²³ suite of program to obtain potential energy, energy gradients and nonadiabatic couplings, on-the-fly. A similar type of direct dynamics trajectory surface hopping (DDTSH) method has been used by us previously in the context of studying bimolecular collision reaction ($O(^3P)+C_2H_2$) with the emphasis of the contribution of intersystem crossing (ISC) dynamics on the product branching.^{32, 33}

Performing MRCISD method with large active space for dynamics calculations is extremely difficult due to its high computational cost. Instead, MRCIS method would be a reasonable choice and it makes dynamics calculations feasible. From the calculation of vertical excitation energies (listed in Table 2) using different chosen active spaces and comparing computed absorption spectrum with that of experimental one (see Fig. 3) we found that active space (6,7) would describe excited potential energy surfaces and couplings reasonably accurate for the photodissociation of propyne. Therefore, we have used MRCIS(6,7)/6-31++G(d,p) level of theory to compute electronic potential energies, gradients and nonadiabatic couplings for studying the photofragmentation dynamics of propyne to keep our calculation simple and feasible. We would like to mention here that increase in the size of the active space hardly improves the accuracy of our calculations.

A three-state state-averaged calculation with equal weights on three low energy singlet states (S_0 , S_1 and S_2) was employed. A batch of 217 trajectories was integrated using the fifth-order Butcher algorithm with a time step of 0.10 fs. For certain trajectories this time step had to be reduced by a factor of 2 to obtain the successive MRCIS calculation converged.

The initial conditions i.e., nuclear coordinates, momenta and starting electronic state are chosen such that a quantum wave packet is mimicked at best (see ref. [22] for details). Unlike simulation of the absorption spectrum, the initial conditions for the trajectories are selected with an energy window of (6.42 ± 0.25) eV to perform the trajectory simulation at 193 nm. Precisely, coordinates and momenta are generated using Wigner distribution function for the ground vibrational state (correspond to zero-point motion in each harmonic normal mode which are imported from Gaussian 09 package²⁸ calculated at the UB3LYP/6-31++G(d,p) level) in the ground electronic state. Each molecular geometry is then accepted or rejected in the excited electronic state based on the ratio of the corresponding transition probability to the maximum transition probability:²²

$$P_{k0} = \frac{(f_{k0}/\Delta E_{k0}^2)}{\max(f_{k0}/\Delta E_{k0}^2)} \quad \text{where } f_{k0} \text{ is the oscillator strength and } \Delta E_{k0} \text{ is the energy gap.}$$

A stochastic algorithm is used for this purpose where the calculated P_{k0} values are compared with the computed random numbers. The momenta of all the atoms in the ground electronic state are used without changing to define initial conditions for the excited state trajectories associated with the S_1 ($^1A''$) state. The trajectory is then propagated in the excited state and Tully's modified "fewest switches" trajectory surface hopping (FS-TSH) algorithm²¹ is employed to compute the transition probability from one potential surface to another for studying the nonadiabatic dynamics. The trajectories were propagated in the adiabatic representation using analytical nonadiabatic (derivative) coupling matrix elements obtained directly from the electronic structure calculations. Once a trajectory jumps, to conserve the total energy the required velocity correction is made along the nonadiabatic coupling vector. Three states, one S_0 ($1^1A'$), and two 1E ($2^1A'$, $1^1A''$) states are included in

the calculation. Transitions between different states are expected when the system is near the avoided intersections. The trajectories were propagated for long enough period of time such that product fragments are separated more than $15 a_0$. However, we did not consider secondary dissociation channels in the present study.

In the present work we have not included the contribution from intersystem crossing (ISC) dynamics induced by spin-orbit coupling between singlet-and triplet states. Along a particular trajectory we have calculated the triplet energies and found that some of the triplet states are even energetically coming below the excited first two singlet states (S_1 , S_2). We however expect that the contribution from ISC will be negligibly small as our calculations showed that the spin-orbit coupling elements are very small (less than 40 cm^{-1}) for alkyne systems.³²

B. TSH results

Our TSH calculations showed that H atom elimination from the acetylenic carbon atom is the major product channel. This finding is in agreement with some of the experimental observations.^{11, 12, 14, 16} Two representative trajectories of this major product channel are shown in Fig. 4. Energies of all the three states included in the calculation are plotted against the time of propagation (upper panel), along with the variation of acetylenic C-H bond distance with the time of propagation (lower panel). From trajectories shown in the upper panel of Fig. 4, it is observed that the dissociation of acetylenic H (indicated by an arrow at a C-H bond distance of $3.0 \text{ \AA}$) takes place within a time range of 18 - 300 fs. The trajectories also reveal that the dissociation takes place in the excited state with no hopping to the ground electronic state up to the dissociation. After the dissociation all the three electronic states (S_0 , S_1

and S_2) become almost degenerate and there are several hopping between them. These hopping are not considered to be real hops as all the three states become degenerate after dissociation. From our trajectory calculations we observed that all the dissociations take place exclusively on the excited state. These observations are in contradiction with the mechanism proposed by Mebel *et al.*¹⁸ where they predicted solely based on electronic structure calculations, without performing dynamics calculations, that the fast dissociation of the acetylenic H proceeds via a nonadiabatic path along the S_1 and S_2 surfaces followed by the $S_2 \rightarrow S_0$ and elimination of the H atom giving H_3CCC . Our findings are however, in accord with the prediction of Ni *et al.*¹⁴ where they proposed based on vacuum ultraviolet detection of products that the excited propyne would mostly be dissociated in the excited electronic state.

The probability of the elimination of H atom from the methyl fragment (channel (2)) is much smaller despite weaker methyl C-H bond compared to acetylenic C-H bond. This is presumably because of the vertical excitation $S_0 \rightarrow {}^1E$ at 193 nm involves excitation of the normal modes corresponding to C-C-C and C-C-H bending and C-H stretching of the acetylenic hydrogen, while the methyl fragment remains almost unaffected.¹⁸ If, at all, H atom elimination has to occur from the methyl fragment, the excitation energy is needed to be transferred to the normal mode which involves C-H stretching of the methyl moiety through the C-C-C bending. Our trajectory calculations indicate that this energy transfer process is too slow to compete with the fragmentation of acetylenic H atom. This is also in agreement with the fact that H atom elimination from methyl moiety has to pass over the transition state TS1 (see Fig. 2(a)) and has to compete with a barrierless acetylenic H atom elimination process in the first excited singlet state (S_1).

From our trajectory propagation we found that none of the trajectories ending into the molecular H₂ elimination channels (channel (3) or (4)). This can be anticipated from the fact that the H₂ elimination processes involve transition states, TS3(S₁) and TS4(S₁) shown in Fig. 2(b), whose energy are comparable to the total available energy of 148.14 kcal/mol. These channels therefore, cannot compete with other channels which have less or almost no barrier to dissociation. This finding is consistent with the branching ratio H:H₂ = 9:1 observed experimentally through primary dissociation processes at 193 nm.¹⁷

We observed less but significant number of trajectories leading to CH₃ + CCH products channel through C—C bond cleavage. Two of the trajectories are plotted in Fig. 5, along with C—C bond distance vs time (fs) plot. It is evident from Fig. 5 that C—C dissociation takes place in the excited singlet state. It is worth pointing out here that none of the experimental studies reported this channel when propyne is photoexcited at 193 nm.

Our trajectory calculations does not give any indication of CH₂+ C₂H₂ products formation through C—C bond cleavage. The CH₂ + C₂H₂ fragments however, were identified at 193 nm with very low quantum yield¹² and were also detected by Ni *et al.*¹⁴ from a very small peak (too weak to be analysed further) in the TOF spectra observed at mass 14.

We have calculated a product translational energy distribution for the major product channel H₃CCC + H from our trajectory calculations and shown in Fig. 6. It is

discernible from the figure that the product translation energy distribution is wide with a maximum at ~ 18 kcal/mol. This distribution indicates that the acetylenic H atom dissociation occurs adiabatically on a moderately repulsive excited surface that correlates with the ground state products, $\text{CH}_3\text{C}\equiv\text{C} + \text{H}$. While our finding supports the observation of some of the earlier experimental observations,^{11, 12, 14, 16} it contradicts a most recent study by Neumark and co-workers.¹⁷ It was proposed, based on a very narrow peak at ~ 5 kcal/mol in the product translation energy distribution, that propargyl radical(channel 2) is the dominating H atom dissociation channel. They, however, did not rule out the formation of propenyl radical (channel 1) with H atom elimination process in the excited surface adiabatically, which might also be consistent with their measured product translation energy distribution.

IV. Conclusion

In the present work we have demonstrated the photodissociation dynamics of propyne at 193 nm using direct dynamics trajectory surface hopping method. Our calculations are based on the MRCIS(6,7) method to obtain potential energies, gradients and nonadiabatic coupling elements. At 193 nm, we found $\text{H} + \text{CH}_3\text{CC}$ is the major fragmentation channel which involves dissociation of acetylenic H. Our dynamics results indicate that this dissociation almost exclusively takes place in the first excited state which is in accord with a recent experimental observation reported by Ni *et al.*¹⁴ Our findings contradict with earlier theoretical prediction of Mebel *et al.*¹⁸ where they proposed that fast acetylenic H atom dissociation takes place through a nonadiabatic path along the S_1 and S_2 surfaces followed by the $\text{S}_2 \rightarrow \text{S}_0$ transition and elimination of the H atom giving H_3CCC in the ground electronic state. It is worth pointing out here that this prediction was solely based on electronic structure

calculation of the stationary points along the reaction path and looking at the similarity of the excited state potential energy surfaces of propyne with that of acetylene reported by Morokuma and coworkers.¹⁹

Our trajectory calculations revealed that the acetylenic H atom dissociation takes place in the excited surface with a product translational energy distribution peaked at around 18 kcal/mol. These findings contradict a most recent experimental observation reported by Robinson *et al.*¹⁷ where they found a narrow product translation energy distribution with a maximum at ~5 kcal/mol. Based on their measured product translation energy distribution it was predicted that the H atom dissociation occurs through the formation of propergyl radical in the ground state followed by internal conversion $S_1 \rightarrow S_0$. It was difficult however, to rule out the formation of propenyl radical, solely based on the product translation energy distribution.

We observed less but significant number of trajectories ended in the $\text{CH}_3 + \text{CCH}$ products channel. There is no experimental evidence of the formation of these products when propyne is excited at 193 nm.

To address the discrepancies between theory and experiment one should perform time-dependent quantum calculations for nuclear motions also. However, these calculations in the full dimensions for molecules with more than four degrees of freedom are prohibitive. Currently, we are making an attempt to perform time-dependent calculations using time-dependent multiconfiguration Hartree methods

developed by Meyer, Manthe, Cederbaum, and co-workers³⁴⁻³⁶ to study photodissociation dynamics in the reduced dimensions.

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References:

- 1 R. H. Qadiri, E. J. Feltham, N. H. Nahler, R. P. García and M. N. R. Ashfold, *J. Chem. Phys.*, 2003, **119**, 12842.
- 2 J. P. Chieze, G. P. d. Foreu and E. Herbst, *Astrophys. J.*, 1991, **373**, 110.
- 3 P. R. Westmoreland, A. M. Dean, J. B. Howard and J. P. Longwell, *J. Phys. Chem.*, 1989, **93**, 8171.
- 4 J. A. Miller and C. F. Mellius, *Combust. Flame*, 1992, **91**, 21.
- 5 A. V. Alakoz, S. V. Kalenskiĭ, V. G. Promislov, L. E. B. Johansson and A. Winnberg, *Astron. Rep.*, 2002, **46**, 551.
- 6 A. Fahr and A. Nayak, *Chem. Phys.*, 1996, **203**, 351.
- 7 W. A. Payne and L. J. J. Stief, *Chem. Phys.*, 1972, **56**, 3333.
- 8 A. Galli, P. Harteck and R. R. R. Jr., *J. Phys. Chem.*, 1967, **71**, 2919.
- 9 P. Kebarle, *J. Chem. Phys.*, 1963, **39**, 2218.
- 10 L. J. Stief, V. J. D. Carlo and W. A. Payne, *J. Chem. Phys.*, 1971, **54**, 1913.
- 11 S. Satyapal and R. Bersohn, *J. Phys. Chem.*, 1991, **95**, 8004.
- 12 K. Seki and H. Okabe, *J. Phys. Chem.*, 1992, **96**, 3345.
- 13 X. Song, Y. Bao, R. S. Urdahl, J. N. Gosine and W. M. Jackson, *Chem. Phys. Lett.*, 1994, **217**, 216.
- 14 C.-K. Ni, J. D. Huang, Y. T. Chen, A. H. Kung and W. M. Jackson, *J. Chem. Phys.*, 1999, **110**, 3320.
- 15 S. Harich, J. J. Lin, Y. T. Lee and X. Yang, *J. Chem. Phys.*, 2000, **112**, 6656.
- 16 W. Sun, K. Yokoyama, J. C. Robinson, A. G. Suits and D. M. Neumark, *J. Chem. Phys.*, 1999, **110**, 4363.
- 17 J. C. Robinson, N. E. Sveum, S. J. Goncher and D. M. Neumark, *Mol. Phys.*, 2005, **103**, 1765.
- 18 A. M. Mebel, W. M. Jackson, A. H. H. Chang and S. H. Lin, *J. Am. Chem. Soc.*, 1998, **120**, 5751.
- 19 Q. Cui, K. Morokuma and J. F. Stanton, *Chem. Phys. Lett.*, 1996, **263**, 46.
- 20 J. C. Tully, *J. Chem. Phys.*, 1990, **93**, 1061.
- 21 S. Hammes-Schiffer and J. C. Tully, *J. Chem. Phys.*, 1994, **101**, 4657.
- 22 G. Barbatti, G. Granucci, M. Persico, M. Ruckebauer, M. Vazdar, M. Eckert-Maksic and H. Lischka, *J. Photochem. Photobiol., A*, 2007, **190**, 228.

- 23 H. Lischka, R. Shepard, I. Shavitt, R. M. Pitzer, M. Dallos and others, Release 5.9.1 edn., 2006.
- 24 H.-J. Werner and P. J. Knowles, *J. Chem. Phys.*, 1998, **89**, 5803.
- 25 P. J. Knowles and H.-J. Werner, *Theor. Chim. Acta*, 1992, **84**, 95
- 26 R. Ditchfield, W. J. Hehre and J. A. Pople, *J. Chem. Phys.*, 1971, **54** 724.
- 27 W. J. Hehre, R. Ditchfield and J. A. Pople, *J. Chem. Phys.*, 1972, **56**, 2257.
- 28 M. J. Frisch, G. W. Trucks, H. B. Schlegel and others, Gaussian 09, Revision C.01, Gaussian, Inc., Wallingford CT, 2010.
- 29 H.-J. Werner, P. J. Knowles, G. Knizia, F. R. Manby, M. Schütz and others, version 2012.1 edn.
- 30 R. Crespo-Otero and M. Barbatti, *Theor. Chem. Acc.*, 2012, **131**, 1237.
- 31 T. Nakayama and K. Watanabe, *J. Chem. Phys.*, 1964, **40**, 558.
- 32 K. Rajak and B. Maiti, *J. Chem. Phys.*, 2010, **133**, 011101.
- 33 K. Rajak and B. Maiti, *J. Chem. Phys.*, 2014, **140**, 044314.
- 34 I. Burghardt, H. D. Meyer and L. S. Cederbaum, *J. Chem. Phys.*, 1999, **111**, 2927.
- 35 G. A. Worth, H. D. Meyer and L. S. Cederbaum, *J. Chem. Phys.*, 1998, **109**, 3518.
- 36 U. Manthe, H. D. Meyer and L. S. Cederbaum, *J. Chem. Phys.*, 1992, **97**, 3199.

Table 1 Geometrical parameters of the equilibrium structure of propyne obtained at the different levels of theory using the 6-31++G(d,p) basis set.

Parameters	UB3LYP	MRCIS(6,7)	MRCISD(6,7)
C-C bond distance	1.457 Å	1.456 Å	1.467 Å
C≡C bond distance	1.202 Å	1.217 Å	1.218 Å
C-C≡C bond angle	179.98°	179.80°	179.99°
C-H bond distance (acetylenic)	1.062 Å	1.058 Å	1.060 Å
C-H bond distance (methyl)	1.094 Å	1.085 Å	1.093 Å

Table 2 Vertical excitation energies (eV) for three low energy excited singlet states of propyne obtained with different electronic structure methods using the 6-31++G(d,p) basis set. Corresponding oscillator strengths are also incorporated in the table using square brackets.

States	CASSCF (6,7)	MRCIS (6,7)	MRCIS (8,8)	MRCIS (8,9)	MRCIS (8,10)	MRCISD (6,7)
1¹A'	6.60 [0.033055]	6.78 [0.036978]	6.72 [0.018624]	6.73 [0.018865]	6.79 [0.020831]	7.09 [0.037906]
2¹A'	6.61 [0.081429]	6.82 [0.049296]	6.72 [0.018621]	6.80 [0.022823]	6.86 [0.025280]	7.10 [0.052231]
1¹A''	7.09 [0.000207]	7.25 [0.000318]	7.41 [0.013886]	7.44 [0.013086]	7.50 [0.011868]	7.34 [0.000406]

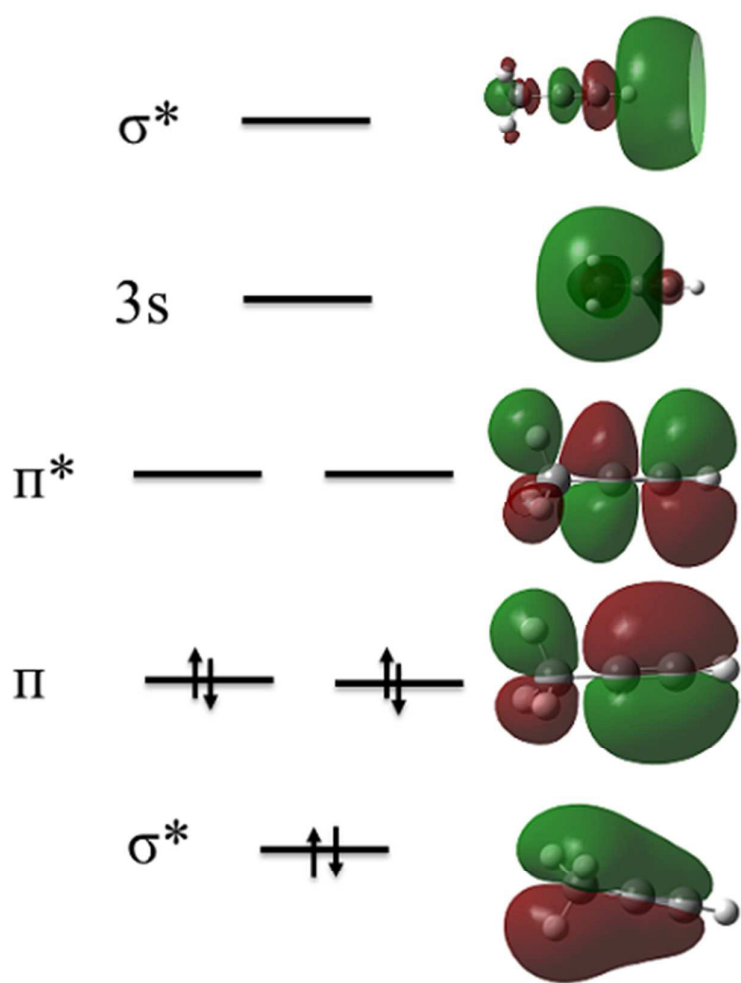


Fig. 1 Shapes of the active orbitals of the active space (6E,7O) used in our calculation.

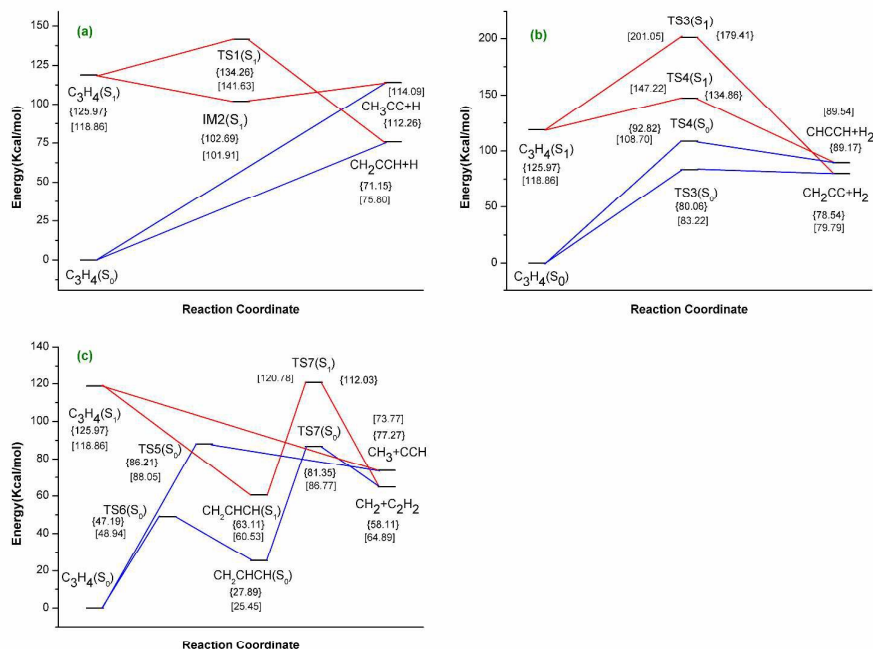


Fig. 2 Potential energy diagrams for the dissociation of propyne to (a) $C_3H_3 + H$, (b) $C_3H_2 + H_2$, (c) $CH_3 + CCH$ and $CH_2 + C_2H_2$. Energy values obtained at the MRCIS(6,7)/6-31++G(d,p) level are shown in curly brackets and at the MRCISD(6,7)/6-31++G(d,p) level in square brackets. All the energy values (reported in kcal/mol) are zero-point energy corrected.

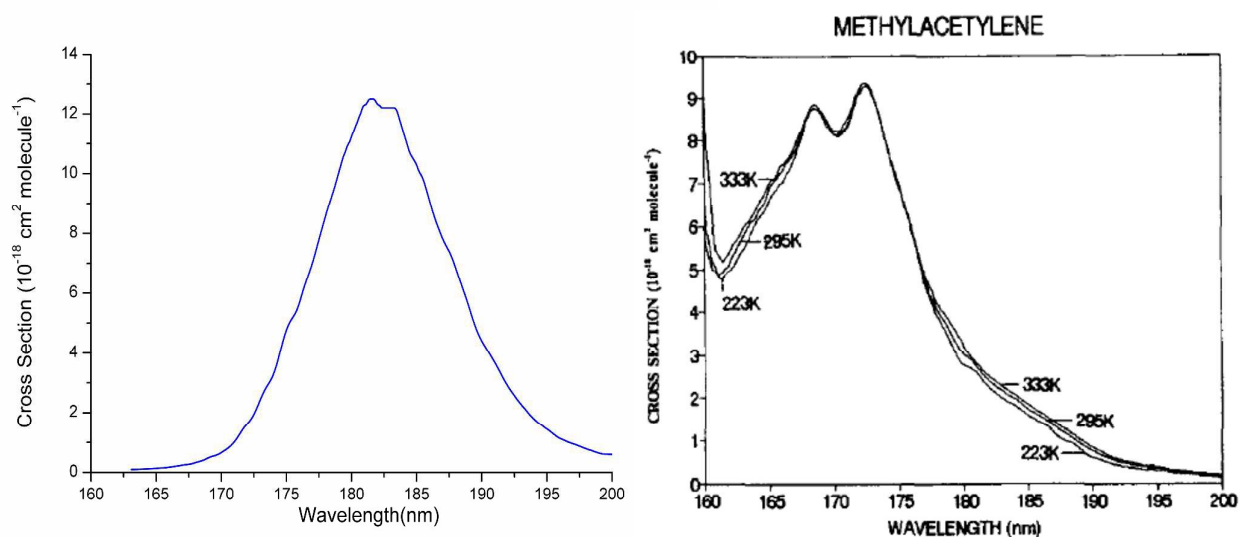


Fig. 3 Absorption spectrum of propyne: (a) computed at the MRCIS(6,7)/6-31++G(d,p) level of theory, (b) observed experimentally, reprinted from Ref. [6].

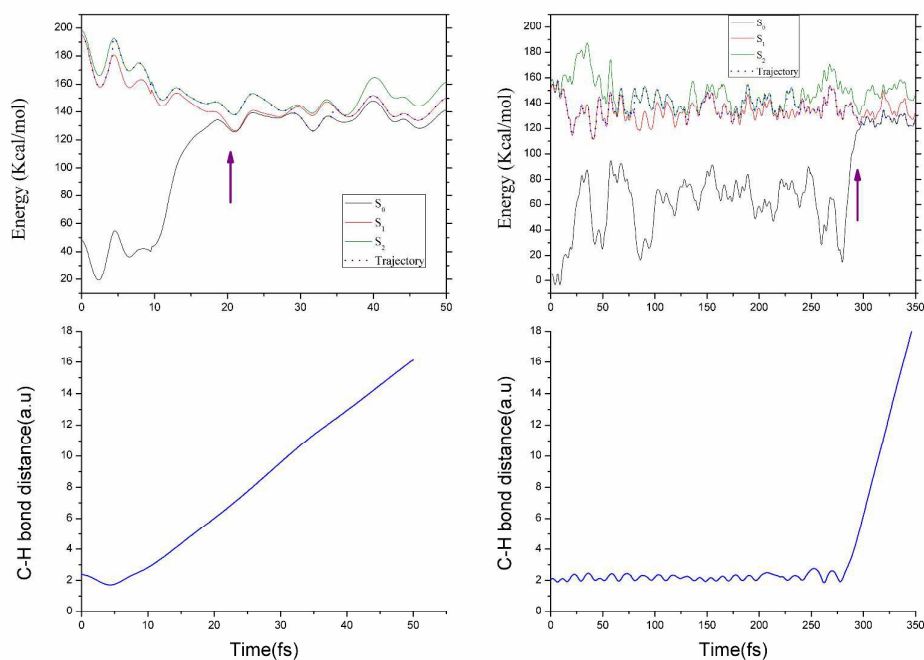


Fig. 4 Upper panel: Evolution of two representative trajectories producing $\text{CH}_3\text{CC} + \text{H}$, computed using DDTSH method with three-state state-averaged MRCIS(6,7)/6-31++G(d,p) method. The energy values are relative to the equilibrium geometry of propyne. Lower panel: Corresponding acetylenic C – H bond distance (a_0) vs. time (fs) plot for the two trajectories. Arrow indicates the dissociation point.

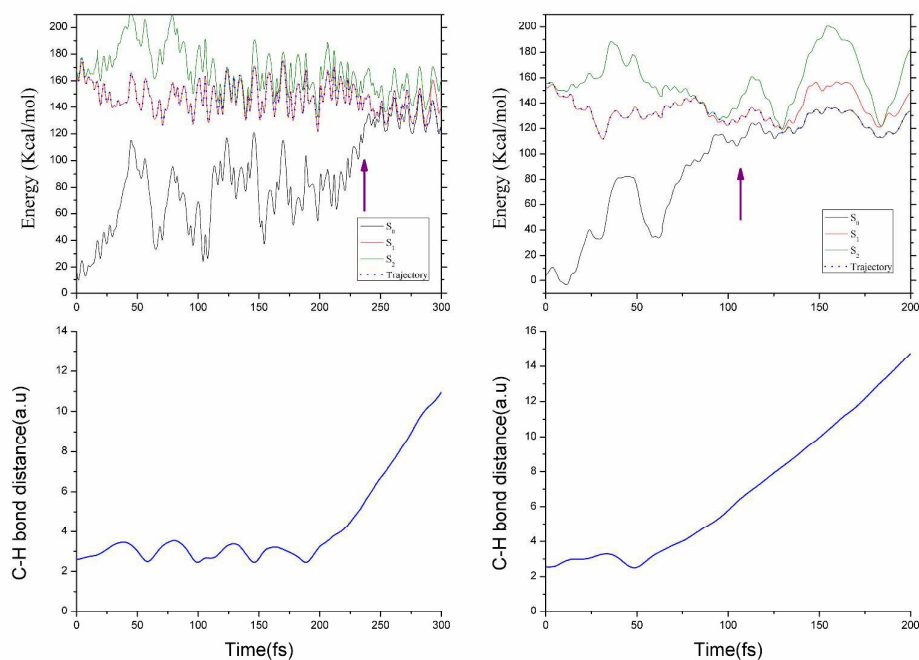


Fig. 5 Upper panel: Evolution of two representative trajectories producing $\text{CH}_3 + \text{CCH}$, computed using DDTSH method with three-state state-averaged MRCIS(6,7)/6-31++G(d,p) method. The energy values are relative to the equilibrium geometry of propyne. Lower panel: Corresponding C – C bond distance (a_0) vs. time (fs) plot for the two trajectories. Arrow indicates the dissociation point.

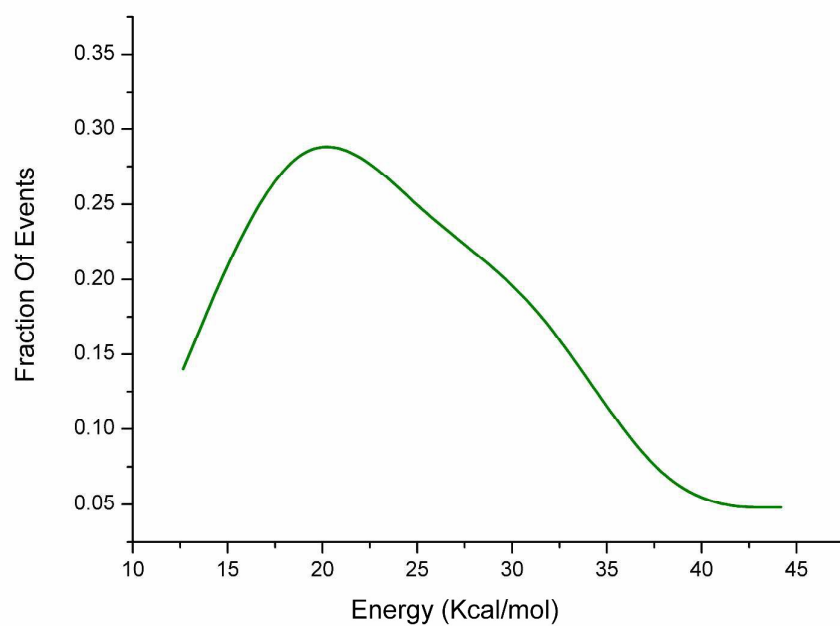


Fig. 6 Product translational energy distribution for the channel $\text{H} + \text{H}_3\text{CCC}$.