

## REGULAR ARTICLE

# Quasiclassical Trajectory Calculations of the Photodissociation of CH<sub>3</sub>CHO: the HCCH + H<sub>2</sub>O Product Channel

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**Abstract:** The photodissociation of the acetaldehyde molecule has been studied based on the quasiclassical trajectory calculations using a global *ab initio*-based potential energy surface. Out of many products channels, the minor channel producing water plus acetylene has been studied. The distributions of the internal energies of the two products, and the relative translational energy have been presented and examined in detail. The distributions are ascribed to the sum of two components corresponding to two reaction pathways, respectively. One pathway is the direct dissociation giving colder HCCH and hotter H<sub>2</sub>O. The other is the dissociation via the vinylidene intermediate giving hotter HCCH and colder H<sub>2</sub>O.

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**Key words:** acetaldehyde, vinylidene, energy distribution, quasiclassical trajectory

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## 1 Introduction

The acetaldehyde molecule is of great importance in combustion chemistry, and in the nature and polluted troposphere. The photodissociation of the acetaldehyde molecule has been

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studied for decades. The photodissociation process generally involves three electronic states, the ground state  $S_0$ , the first excited singlet state,  $S_1$ , and the first triplet state,  $T_1$ . Briefly speaking, the acetaldehyde molecules are initially excited from the  $S_0$  state to the  $S_1$  state. Starting from the  $S_1$  state, the molecules can return to the  $S_0$  state via internal conversion, or to the  $T_1$  state via intersystem crossing. The resulting energetic molecules can then dissociate on the  $S_0$  state to form multiple product channels. The dissociation can also occur on the  $T_1$  state to form the radical products,  $\text{CH}_3 + \text{HCO}$ ; however, this process is not of further interest here.

The two major product channels, the molecule products  $\text{CH}_4 + \text{CO}$  and the radical products  $\text{CH}_3 + \text{HCO}$ , on the  $S_0$  state in the dissociation dynamics of the acetaldehyde molecules have been studied extensively [1-26]. Kurosaki and Yokoyama performed direct-dynamics quasiclassical trajectory (QCT) calculations of the photodissociation dynamics focusing on the  $\text{CH}_4 + \text{CO}$  channel [17, 18] and on some other product channels [19, 20]. The roaming mechanism in the formation of the  $\text{CH}_4 + \text{CO}$  channel is one of the most interesting aspects in the study of the photodissociation dynamics. The "roaming" mechanism known as an alternative pathway, with respect to the conventional transition state theory pathway, has first been discovered in the photodissociation of the formaldehyde molecules [26]. The photodissociation of the acetaldehyde to  $\text{CH}_4 + \text{CO}$  has been named as the second example for the roaming mechanism [21-25].

The high-energy photolysis or the thermal decomposition is another interesting aspect in the study of the dissociation of the acetaldehyde molecules. Recently, Lee [10] reported the high-energy photolysis experiments at 157 nm, in which numerous products with  $\text{CH}_3 + \text{CO} + \text{H}$  accounting for approximately half of the total branching have been observed. Vasiliou et al. [12] reported the thermal decomposition of  $\text{CH}_3\text{CHO}$  at 1700 K, where the decomposition products included  $\text{CH}_3$ ,  $\text{CO}$ ,  $\text{H}$ ,  $\text{H}_2$ ,  $\text{CH}_2\text{CO}$ ,  $\text{CH}_2\text{CHOH}$ , and  $\text{H}_2\text{O} + \text{C}_2\text{H}_2$ . They also proposed that the water plus acetylene products are formed via two pathways: one that produces these products directly, and a very interesting one that first produces water plus vinylidene, and the vinylidene then isomerizes to the acetylene. These proposed pathways are analogous to ones reported in recent dynamics calculations of the unimolecular dissociation of the allyl radical to form  $\text{CH}_3 + \text{C}_2\text{H}_2$  [27,28]. Stimulated by these experiments, we presented a quasiclassical trajectory study of the photodissociation of  $\text{CH}_3\text{CHO}$  using a global *ab initio*-based potential energy surface [29]. Calculations are performed at a total energy of 160 kcal/mol, corresponding to a photolysis wavelength of 230 nm. Various product channels have been found at this high energy, which are in agreement with the experimental thermal decomposition findings at 1700 K. We have also identified the two pathways producing water accompanied by acetylene or vinylidene with the intermediate vinyl alcohol:

