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REGULAR ARTICLE

Quasiclassical Trajectory Calculations of the Photodissociation of CH_3CHO: the HCCH + H_2O 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_2O. The other is the dissociation via the vinylidene intermediate giving hotter HCCH and colder H_2O.

AMS subject classifications: 37M05, 35F45, 65M22

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

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 S0, the first excited singlet state, S1, and the first triplet state, T1. Briefly speaking, the acetaldehyde molecules are initially excited from the S0 state to the S1 state. Starting from the S1 state, the molecules can return to the S0 state via internal conversion, or to the T1 state via intersystem crossing. The resulting energetic molecules can then dissociate on the S0 state to form multiple product channels. The dissociation can also occur on the T1 state to form the radical products, CH_3 + HCO; however, this process is not of further interest here.

The two major product channels, the molecule products CH_4 + CO and the radical products CH_3 + HCO, on the S0 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 CH_4 + CO channel [17, 18] and on some other product channels [19, 20]. The roaming mechanism in the formation of the CH_4 + 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 CH_4 + 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 CH_3 + CO + H accounting for approximately half of the total branching have been observed. Vasiliou et al. [12] reported the thermal decomposition of CH_3CHO at 1700 K, where the decomposition products included CH_3, CO, H, H_2, CH_2CO, CH_2CHOH, and H_2O + C_2H_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 CH_3 + C_2H_2 [27,28]. Stimulated by these experiments, we presented a quasiclassical trajectory study of the photodissociation of CH_3CHO 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:

$$CH_3CHO \rightarrow CH_2CHOH \rightarrow HCCH + H_2O \tag{1.1}$$

$$CH_3CHO \rightarrow CH_2CHOH \rightarrow [H_2CC] + H_2O \rightarrow HCCH + H_2O \quad (1.2)$$

In this paper, as an extension of Ref. [29], we focus on the two pathways producing the $HCCH + H_2O$ products. We are stimulated by the question how these two pathways affect on the final energy distributions of the products. Based on the quasiclassical trajectory calculations on the full-dimensional *ab initio*-based potential energy surface, we calculated the internal energy distributions and the relative translational energy distribution, and examined them in detail.

The paper is organized as follows. The full-dimensional potential energy surface is briefly described in the next section. The QCT method and the corresponding results have been presented and discussed in detail in Section 3. The conclusions have been summarized in Section 4.

2 Potential Energy Surface

In the previous calculations of CH_3CHO dissociation [23, 24], we employed two PESs, which were fits to roughly 170 000 *ab initio* energies. These energies were calculated at the CCSD(T)/AVTZ level of theory. The PESs can describe the complex regions and the fragments of all possible channels. To improve the accuracy of the previous PESs, we performed MRCI/VTZ calculations in the open-shell complex region like $CH_3\bullet\bullet\bullet HCO$, $CH_3CO\bullet\bullet\bullet H$; MRCI/AVTZ calculations in the biradical ($\bullet CH_2CH_2O\bullet$) region; and CCSD(T)/AVTZ calculations in the vinyl alcohol and hydroxyethylidene regions. Both the MRCI/VTZ and MRCI/AVTZ energies are properly shifted before being added to the CCSD(T)/AVTZ data base. All these added energies were obtained with MOLPRO [30]. Currently, the entire data set of roughly 200 000 energies was fit, as before, using a basis of permutationally invariant polynomial in Morse-like variables in all the inter-nuclear distances. The fit is of maximum fifth order and has an rms fitting error of 2.9 kcal/mol, for energies up to 160 kcal/mol above the CH_3CHO minimum. The fit, which we refer to henceforth as the potential energy surface (PES) describes stationary points of complex region and fragment channels very well. The detail descriptions of constructing the global *ab initio* potential energy surface can be referred to Ref. [29].

The energy profile of the stationary points and fragment channels is shown in **Figure 1**. The relative two pathways to form the $HCCH+H_2O$ products have been marked as red. As shown in **Figure 1**, there are two pathways for the vinyl alcohol to dissociate into the water and acetylene. One is via TS7 (~93.5 kcal/mol) to form acetylene and water directly, corresponding to (1.1); the other one is via TS6 (~95.6 kcal/mol) to form vinylidene and water first, and then the vinylidene isomerizes to acetylene, i.e. (1.2). Other possible dissociation channels have been marked as blue. The isomerization pathways between the acetaldehyde global minimum and other local minima have been marked as black.

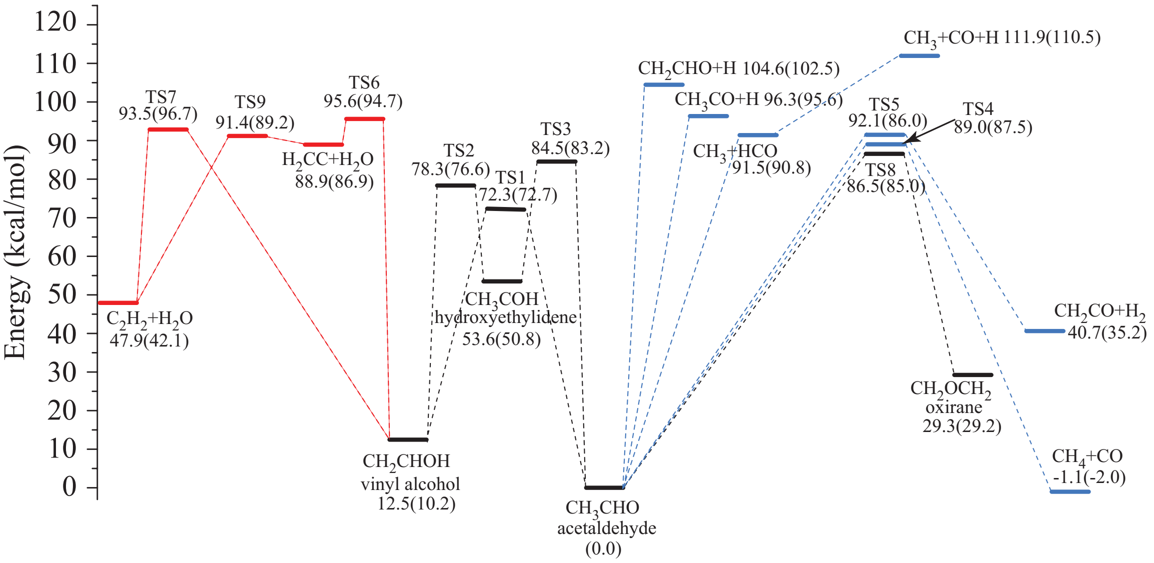

Figure 1: Schematic of stationary points of relevance to the present dynamics calculations of dissociation of CH_3CHO. The fitted energies are in kcal/mol, relative to the global minimum acetaldehyde, and those shown in parentheses are from CCSD(T) /AVTZ calculations. The black lines denote the isomerization pathways, and the blue lines represent the dissociation pathways. The red lines denote the concerning H_2O + C_2H_2 and H_2CC channels.

3 Results and discussion

The QCT calculations were carried out starting at the CH_3CHO global minimum with the total energies of 160.0 kcal/mol, which is the sum of the (harmonic) CH_3CHO zero-point energy and the photon energy of 124.0 kcal/mol (i.e., 230 nm). The total angular momentum was fixed at zero. Random microcanonical sampling of the Cartesian momenta in all degrees of freedom was done to generate initial conditions, subject to the constraint of zero total angular and linear momentum, as described in detail previously [22-24]. The time step is 0.12 fs and the trajectories were integrated for a maximum of 10 million time steps (1.2 ns). 24800 trajectories have been run and roughly 1% dissociated into the HCCH + H_2O.

We took these trajectories into consideration, since we are interested in this product channel. As mentioned above, the HCCH + H_2O products result from the two pathways, (1.1) and (1.2). In both pathways, the dissociation starts from the vinyl alcohol (CH_2CHOH) which is one of the most important isomers of acetaldehyde. We picked up two trajectories that produce water plus acetylene in different pathways: One is via vinyl alcohol direct dissociation [i.e., (1.1)], and the other one is via vinylidene isomerization [i.e., (1.2)]. The snapshots of these two trajectories are shown in **Figure 2**. The dissociation from vinyl alcohol directly to acetylene is shown in the left panels, and the dissociation from vinyl alcohol to vinylidene (H_2CC) which then isomerized to acetylene is shown in the right panels.

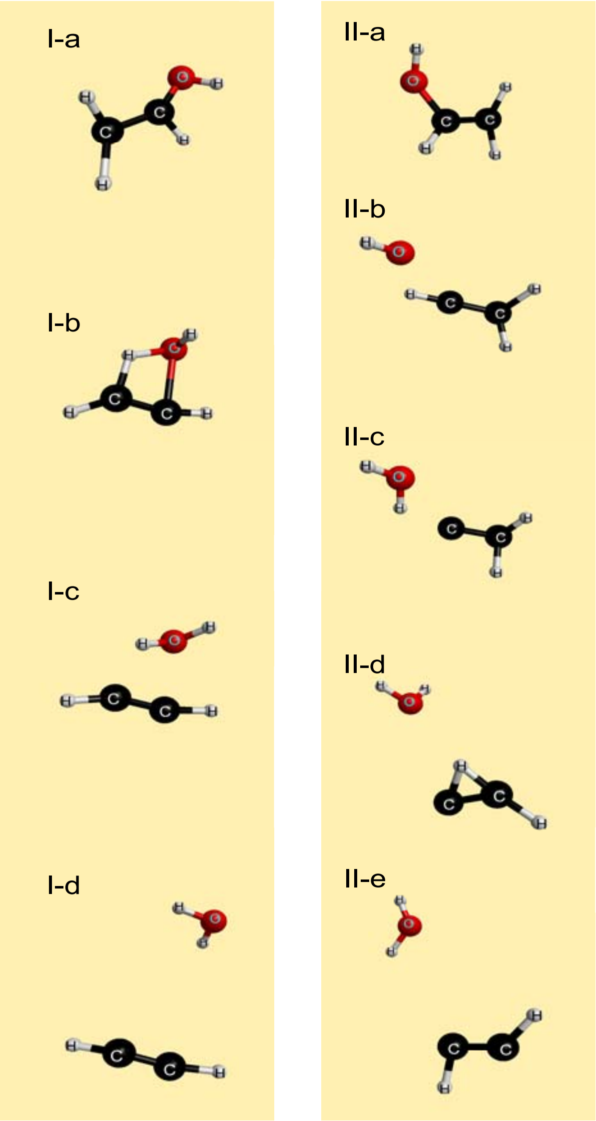

Figure 2: Snapshots of the two trajectories producing the acetylene plus water via two different pathways. Left panels show the direct dissociation from the vinyl alcohol to the acetylene and water corresponding to (1.1), and right panels show the dissociation from vinyl alcohol first to water and vinylidene, and the later isomerization from vinylidene to acetylene according to (1.2).

To form acetylene directly via TS7, the OH group and the H atom eliminate from the different Carbon atoms named as (1,2)-elimination, while to form vinylidene via TS6, the OH group and the H atom eliminate from the same side of Carbon which can be called (1,1)-elimination. Because the barrier height of TS7 is energetically similar to TS6, the branching ratios of the two pathways are expected to be comparable. As well known, there is a quite small barrier TS9 (roughly 2.3 kcal/mol above the vinylidene local minimum) for the vinylidene isomerizing to the acetylene [34-41]. It can be expected that those acetylene isomerized from the vinylidene can be highly excited, because of the high internal energy of vinylidene. As shown in **Figure 1**, the dissociation limit on the PES for $H_2CC + H_2O$ is about 88.9 kcal/mol while that for HCCH + H_2O is about 47.9 kcal/mol. For these two trajectories we shown in **Figure 2**, the final internal energy of acetylene that produced via H_2CC is roughly 72 kcal/mol, which is much higher than the acetylene directly produced via vinyl alcohol (26.8 kcal/mol).

To further investigate the contributions of the two pathways to the final energy distributions, we calculated the internal energy distributions of HCCH and H_2O, respectively, and also the relative translational energy distribution. The internal energy distribution of HCCH is shown in **Figure 3**. The black line shows the total distribution taking all of the HCCH products into account. As seen, the internal energy of the HCCH products distributed in a broad energy region, from roughly 10 to roughly 105 kcal/mol. Note that there is a small amount of the acetylene molecules below the zero point energy (ZPE) 16 kcal/mol. This small unphysical distribution is caused by "ZPE-leak", a well-known issue in QCT calculations, which results from the classical intramolecular vibrational relaxation of the harmonic ZPE from the high-frequency modes to lower-frequency ones.

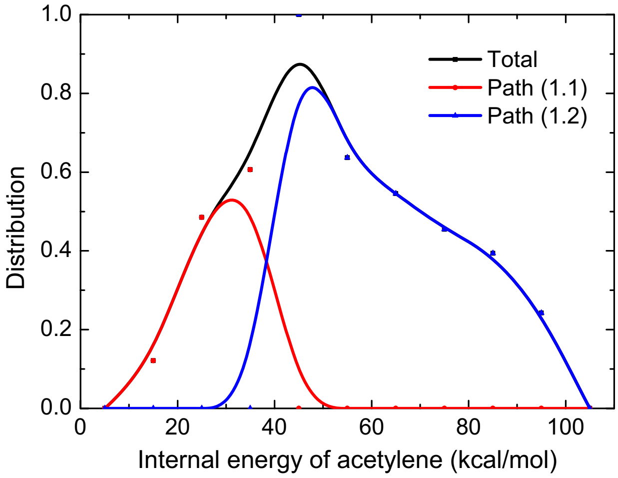

Figure 3: The internal energy distribution of the acetylene products.

We then divided the above distribution into two components, according to the two different pathways. As seen in **Figure 3**, the red line is the component from the direct-dissociation pathway, (1.1), and the blue line is the component from the "vinylidene"-intermediate pathway, (1.2). The distributions of the two components are quite different. First, the internal energy of the acetylene generated from the pathway (1.1), is quite smaller than those from the pathway (1.2). Second, the yield of the acetylene from the pathway (1.2) is greater than that from (1.1). These two points are in agreement with our expectations based on the analysis of the potential energy surface.

Moreover, we performed the similar analysis to the internal energy distributions of the water products. As shown in **Figure 4**, the internal energy distributions from the two components also present somewhat different. The water products generated via pathway (1.1), peaking at roughly 25 kcal/mol, is a little colder than those generated via the pathway (1.2), peaking at roughly 35 kcal/mol.

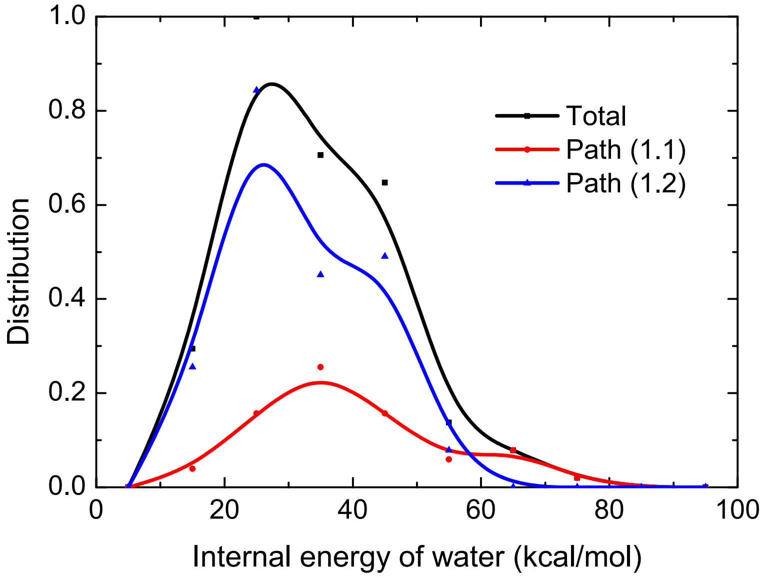

Figure 4: The internal energy distribution of the water products.

The relative translational energy distribution is shown in **Figure 5**. Accordingly, the total distribution in the black line is also divided into the two components; the red and blue lines correspond to pathways (1.1) and (1.2), respectively. The translational energy distribution for the products from pathway (1.1), is a broad one, centered at 45 kcal/mol. This is a typical translational energy distribution for the dissociation passing a transition state barrier. The distribution for the products from pathway (1.2), is quite different. It declines with the increase of the translational energy. This is similar to the typical distribution for the products from a barrierless dissociation path. This is because the transition state TS6 is energetically close to the product channel of the vinylidene plus water. The bare energy difference between the two stationary points on the PES is roughly 6.7 kcal/mol, which is much smaller than the barrier height 95.6 kcal/mol. Thus, the translational energy distribution for the products from the "vinylidene-intermediate" pathway, is somewhat like that from a barrierless reaction pathway.

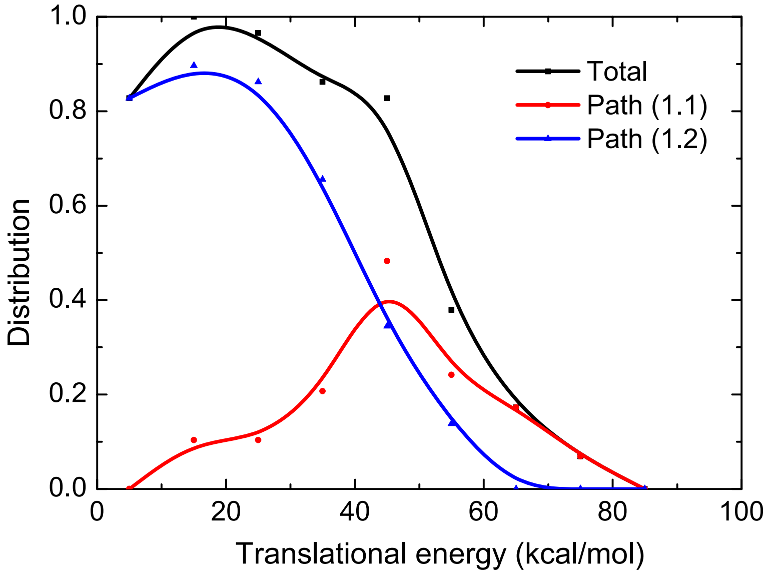

Figure 5: The relative translational energy distribution of the final water plus acetylene products.

4 Conclusions

In summary, we performed quasiclassical trajectory calculations of the photodissociation of the acetaldehyde molecule using a global *ab initio*-based potential energy surface. The total energy is set to be 160 kcal/mol, corresponding to a photolysis wavelength of 230 nm. In this work, we mainly focused on the interesting minor channel, producing water plus acetylene, although there are many other product channels. To form the acetylene and water products, the acetaldehyde molecule first isomerized to vinyl alcohol. Then starting from the vinyl alcohol isomer, the dissociation can pass two difference pathways to the final HCCH + H_2O products. One is the direct dissociation, and the other is the dissociation via the vinylidene intermediate.

The internal energy distributions of the final two products, acetylene and water, and the relative translational energy distributions have been investigated. The energy distributions are ascribed to the sum of the two components according to the two reaction pathways, respectively. The direct dissociation pathway results in the colder HCCH and a little bit hotter H_2O, while the other gives hotter HCCH and colder H_2O. Also the translational energy distributions from the pathways show different features. The direct dissociation pathway leads to a typical transition state distribution, a broad one with a central peak. The "vinylidene-intermediate" pathway however leads to a barrierless-like dissociation distribution.

Acknowledgments

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