Molecular dynamics of methanol cation (CH$_3$OH$^+$) in strong fields: Comparison of 800 nm and 7 μm laser fields

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ARTICLE INFO

ABSTRACT

Fragmentation and isomerization of methanol cation by short, intense laser pulses were studied by ab initio classical trajectory simulations using CAM-B3LYP/6-31G(d,p) calculations. Compared to random orientation, CH$_3$OH$^+$ with the C—O bond aligned with the laser polarization gained nearly twice as much energy from the laser field, in accordance with the higher vibrational intensities in the mid-IR range for aligned CH$_3$OH$^+$. The energy gained by CH$_3$OH$^+$ from 7 μm and 800 nm laser pulses with intensities of 0.88×10^{14} and 1.7×10^{14} W/cm^2 is proportional to the intensity and the wavelength squared of the laser field.

1. Introduction

In recent work, Yamanouchi and co-workers used intense 800 nm laser pulses to study the fragmentation of methanol cations [1–8]. Through the use of coincidence momentum imaging they were able to examine hydrogen ejection processes for the dication, CH$_3$OH$^{2+} \rightarrow$ CH$_{3-n}$OH$^+ +$ H$_n^+$ and to determine that hydrogen migration, CH$_3$OH$^{2+} \rightarrow$ CH$_2$OH$_2^{2+}$, occurred in within the laser pulse. Pump-probe coincidence momentum imaging revealed that ultrafast hydrogen migration also occurred in the monocation [7,8]. In a recent study, we used ab initio classical trajectory calculations to investigate the dynamics of methanol monocation on the ground state potential energy surface in the presence of a strong laser field [9]. At 800 nm, the classical dynamics simulations showed that ground state methanol cation gained very little energy from the laser field. By adding a significant amount of vibrational energy, we were able to model the fragmentation and isomerization of methanol cation. This implied that the 800 nm laser pulse deposits its energy by electronic excitation of the cation or by coupled nuclear-electron dynamics. By contrast, in the mid-IR range, we can expect the laser field to interact directly with the molecular vibrations on the ground state potential energy surface of methanol cation. In the present study, we examine the interaction of randomly oriented and aligned methanol cation with intense 7 μm laser pulses and compare the results with the prior dynamics study at 800 nm [9]. In earlier work, we found that intense mid-IR pulses

were able to selectively enhance specific reaction channels for aligned molecules [10,11].

2. Methods

The molecular dynamics of methanol cation were studied using density functional theory on the ground state potential energy surface in the presence of a strong laser field. Electronic structure calculations were carried out using the development version of the Gaussian series of programs [12] with the CAM-B3LYP/6-31G(d,p) level of theory [13] (the CAM-B3LYP functional has 19% HF exchange at short range and 65% HF at long range with a range parameter of 0.33). Classical trajectories were integrated with our Hessian-based predictor–corrector algorithm [14]. In this method, the surface is approximated by a distance weighted interpolant (DWI) using the first and second derivatives of the energy. The first derivatives of the gradient with respect to the electric field are also included in the predictor and the corrector steps. The velocity Verlet method with $\delta t = 0.0025$ fs is used to integrate both the predictor and corrector steps on the DWI surface. An overall step size of $\Delta t = 0.25$ fs is employed and the Hessian is updated [15,16] for 20 steps before being recalculated analytically. The 7 μm laser pulse was modeled by a time varying electric field with a length of four cycles (95 fs) and a trapezoidal envelope (increasing linearly for the first cycle and decreasing linearly for the last cycle). The maximum field strengths were 0.05 au $(0.88 \times 10^{14}$ W/cm^2) and 0.07 au $(1.7 \times 10^{14}$ W/cm^2). The direction of the laser field was chosen to be aligned with the C—O bond axis or oriented randomly. The starting structures had no rotational energy and zero point energy was added to the initial structures using orthant sampling of the

Table 1

Number of trajectories for 7 μm 0.05 and 0.07 au field strength random and aligned, compared with 800 nm 0.07 au random with 314 kJ/mol extra energy.

Field orientation and wavelength	Field strength	$CH_2OH^+ + H$	$HCOH^+ + H_2$	$CH_2OH_2^+$	$CH_3^+ + OH^+$	No reaction	Total	Reaction during pulse	Reaction after pulse
Random 7 μm	0.05 au	58	9	3		129	199	9	61
	0.07 au	92[a]	20[d]	3	1	44	162	37	81
C-O aligned 7 μm	0.05 au	102	29[b]	12		55	198	9	134
	0.07 au	95	42[c]	6	4	13	160	34	113
Random 800 nm (+314 kJ/mol)	0.07 au	111	23	6		22	162	20	120

[a] Two of these trajectories dissociated into $CHO^+ + H + H_2$.

[b] Two of these trajectories dissociated to $CH_2O^+ + H_2$ and one dissociated to $CHO^+ + H_2 + H$.

[c] Six of these trajectories dissociated to $CH_2O^+ + H_2$ and 13 dissociated to $CHO^+ + H_2 + H$.

[d] Four of these trajectories dissociated to $CHO^+ + H_2 + H$.

momentum [17]. Up to 200 trajectories were calculated for each set of starting conditions. A few trajectories dissociated sequentially into multiple fragments; these were classified by the first dissociation event (see Table 1 footnotes). The simulations with the 7 μm laser pulse are compared with previous strong field dynamics calculations with 800 nm laser pulses. As in the case of the 800 nm laser pulse, some of the trajectories integrated with the 7 μm pulse showed an unusually high gain in energy. This problem was traced to an artifactual charge oscillation when the C—H bond stretched to more than 3 Å within the laser pulse. Because the electronic structure was converged at each step of the trajectory integration rather than being propagated, the charge on the hydrogen in the elongated C—H bonds varied from H^+ to $H^\bullet$ to H^- as the field changed sign. These trajectories resulted in a gain of more than 840 kJ/mol (200 kcal/mol) and were discarded as artifacts to the Born–Oppenheimer molecular dynamics approach.

3. Results and discussion

The energetics for the fragmentation of methanol cation have been studied previously at the CBS-APNO, CBS-QB3 and G4 levels of theory and are summarized in Figure 1 [9]. There are three low energy channels: loss of hydrogen to produce CH_2OH^+ (72 kJ/mol), loss of H_2 to produce $HCOH^+$ (131 kJ/mol barrier) and isomerization to $CH_2OH_2^+$ (102 kJ/mol barrier). Higher energy channels include dissociation of the C—O and O—H bonds in CH_3OH^+ (276 and 418 kJ/mol, respectively) and dissociation of the C—O bond in $CH_2OH_2^+$ (294 kJ/mol). The CAM-B3LYP/6-31 G(d,p) calculations are in good agreement with the higher level calculations and, as in

the previous study, are chosen for the trajectory calculations as a compromise between accuracy and efficiency.

The infrared spectrum of methanol cation is shown in Figure 2, both for rotationally averaged CH_3OH^+ and for the C—O axis aligned with the polarization of the laser field. The frequency distribution of a short, intense pulse of 7 μm is centered around 1430 cm^{-1}. This is close to the C—H bending vibrations, and the intensities are significantly higher in this region for the aligned cation than for the rotationally averaged case.

As the laser field interacts with the molecule, considerable energy is deposited in the various vibrational modes. Figure 3 shows the distributions of the amount of energy gained by methanol cation from the 4 cycle 7 μm trapezoidal pulses with field strengths of 0.05 and 0.07 au (0.88×10^{14} and 1.7×10^{14} W/cm^2, respectively). Randomly oriented molecules gain an average of 175 and 338 kJ/mol, Figure 3(a). As expected, the average amount of energy gained is proportional to the intensity of the laser field (i.e. proportional to the square of the field strength). When the C—O bond of methanol cation is aligned with the field polarization, Figure 3(b), the amount of energy gained is nearly doubled, 316 and 504 kJ/mol respectively for field strengths of 0.05 and 0.07 au. This is consistent with the higher vibrational intensities for the aligned molecule. When the wavelength is shortened from 7 μm to 800 nm and methanol cation is restricted to the adiabatic ground state surface, much less energy is absorbed, Figure 3(c) and (d). The averages are 2.3 and 7.8 kJ/mol for randomly oriented CH_3OH^+ and 2.0 and 5.7 kJ/mol for aligned CH_3OH^+ at field strengths of 0.05 and 0.07 au, respectively. Since the ponderomotive energy of a free ion in an oscillating field is proportional to the wavelength squared, one would expect the ratio of the energies to be approximately
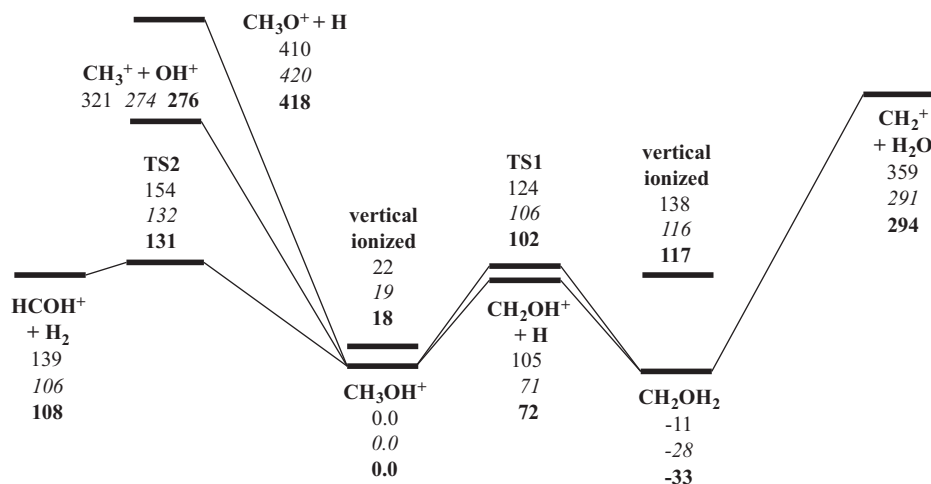

Figure 1. Relative enthalpies at 0 K in kJ/mol for CH_3OH^+ calculated at the CAM-B3LYP/6-31G(d,p), CBS-QB3 (italics) and CBS-APNO (bold) levels of theory
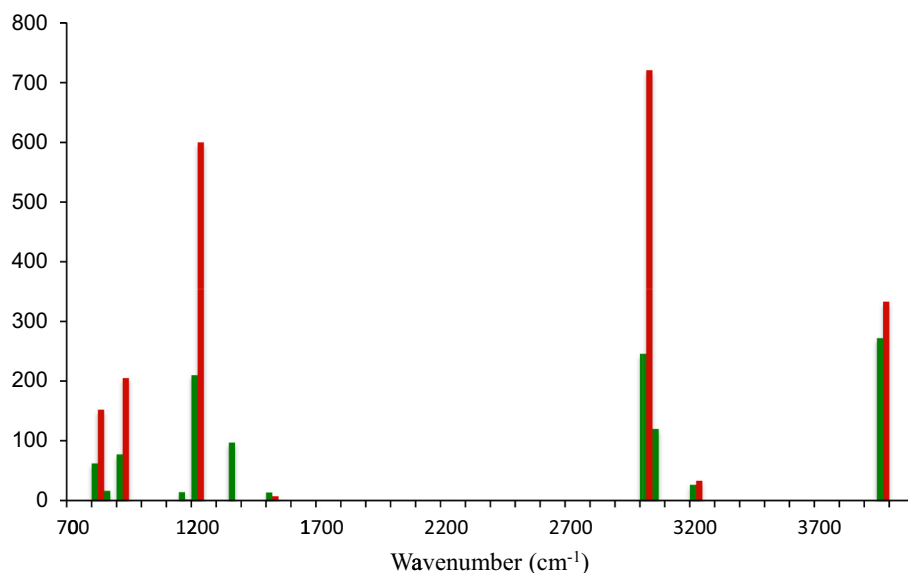Adapted with permission from J. Phys. Chem. A 118 (2014) 1769. Copyright 2014 American Chemical Society.

Figure 2. IR spectrum of CH_3OH^+ (a) rotationally averaged (green), and (b) aligned with the field (red). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this letter.)
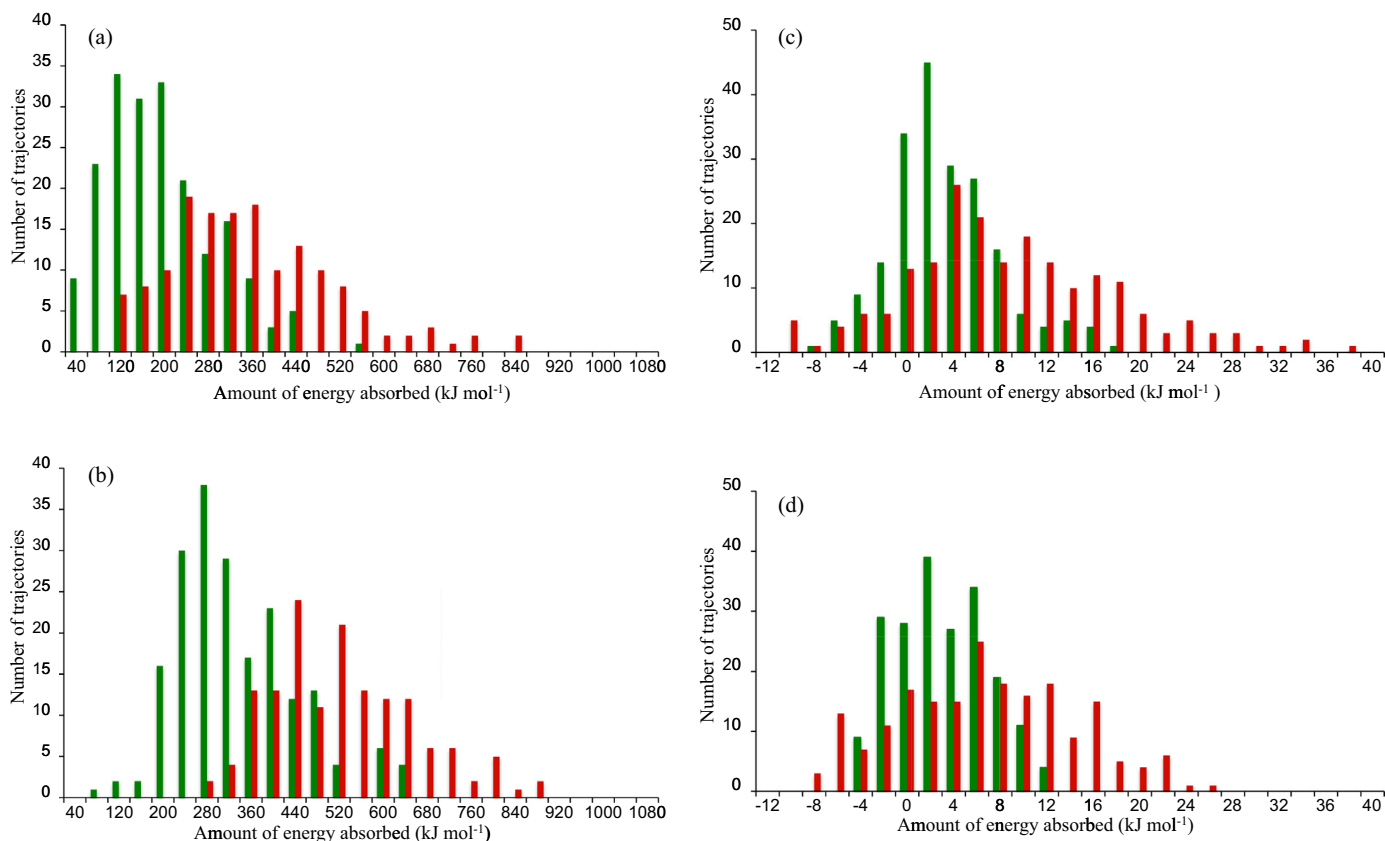

Figure 3. Histograms of the distribution of the vibrational energy absorbed by CH_3OH^+ as a function of molecular orientation and laser wavelength at two different field strengths (0.05 au in green and 0.07 au in red): (a) random orientation 7 μm, (b) CO aligned 7 μm 0.05 au, (c) random orientation 800 nm, and (d) CO aligned 800 nm. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this letter.)

75. This is reasonable agreement with the observed ratios of 43–76 for randomly oriented methanol cation and 87–154 for aligned. The effect of alignment is much greater for the 7 μm pulse because this wavelength is close to resonance with some of the vibrational modes whose intensities are significantly enhanced by alignment.

The results of the trajectory calculations are summarized in Table 1. For a field strength of 0.05 au and random orientation of methanol cation, only a third of the trajectories dissociated or isomerized within 400 fs; most of these dissociated after the pulse. When the field was increased to 0.07 au, nearly three quarters of the trajectories reacted; this also increased the number of trajectories

that reacted during the pulse. The branching ratios for the reactive trajectories were similar for the two field strengths: 78–83% dissociated to $CH_2OH^+ + H$, 13–17% formed $HCOH^+ + H_2$, and 3–4% isomerized to $CH_2OH_2^+$. Only one $CH_3^+ + OH$ dissociation event was seen at 0.07 au field strength out of 162 trajectories. When the C—O bond is aligned with the field, there were significantly fewer nonreactive trajectories for a given field strength, in keeping with the fact that the pulse deposited more energy in the oriented molecule. The percentage of reactive trajectories resulting in H dissociations decreased to 65–71% and the percentage going to H_2 dissociation (20–29%) and isomerization (4–8%) nearly doubled. Alignment also increased the fraction of $CH_3^+ + OH$ dissociations to 4 out of 160.

Simulations on the ground state adiabatic surface with 800 nm laser pulses gained too little energy to isomerize or dissociate. However, strong field pulses at 800 nm probably cause significant excitation of CH_3OH^+. If decay to the ground state is rapid, this excitation energy would be converted to vibrational energy. In our previous paper, we modeled this by adding extra vibrational kinetic energy to the starting structures. With 314 kJ/mol (75 kcal/mol) added energy, the branching ratios with randomly oriented 800 nm pulses and a field strength of 0.07 au were similar to trajectories with randomly oriented 7 μm pulses and 0.07 au field strength. This is in accordance with the fact that CH_3OH^+ gained an average of 338 kJ/mol in the 7 μm pulse.

Summary

Ab initio classical trajectory calculations were used to study the fragmentation and isomerization of methanol cation caused by short, intense laser pulses. The dominant channels are $CH_2OH^+ + H$ (65–83%), $HCOH^+ + H_2$ (13–29%), $CH_2OH_2^+$ (3–8%), and $CH_3^+ + OH$ (0.5–2.5%). For a 4 cycle 7 μm pulse, significant differences were seen in the amount of vibrational energy deposited and the branching ratios when methanol cation was oriented randomly or had its C—O bond aligned with the field. The increased energy deposited

can be understood in terms of the increased vibrational intensities in the mid-IR region when the C—O bond of CH_3OH^+ is aligned with the laser polarization. Randomly oriented methanol cations gain an average of 175 and 338 kJ/mol for 4 cycle 7 μm pulses with intensities of 0.88×10^{14} W/cm^2 and 1.7×10^{14} W/cm^2, respectively, but only 2.3 and 7.8 kJ/mol from 4 cycle 800 nm pulses with the same intensity. This is in agreement with fact that the ponderomotive energy is proportional to the intensity and the wavelength squared of the laser field.

Acknowledgements

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