Molecular Dynamics of Methylamine, Methanol, and Methyl Fluoride Cations in Intense 7 Micron Laser Fields

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ABSTRACT: Fragmentation and isomerization of methylamine (CH₃NH₂⁺), methanol (CH₃OH⁺), and methyl fluoride (CH₃F⁺) cations by short, intense laser pulses have been studied by ab initio classical trajectory calculations. Born–Oppenheimer molecular dynamics (BOMD) on the ground-state potential energy surface were calculated with the CAM-B3LYP/6-31G(d,p) level of theory for the cations in a four-cycle laser pulse with a wavelengths of 7 μm and intensities of 8.8 × 10¹⁴ and 1.7 × 10¹⁴ W/cm². The most abundant reaction path was CH₂X⁺ + H (63–100%), with the second most favorable path being HCX⁺ + H₂ (0–33%), followed by isomerization to CHXH⁺ (0–8%). C–X cleavage after isomerization was observed only in methyl fluoride. Compared to random orientation, CH₃X⁺ with the C–X aligned with the laser polarization gained energy nearly twice as much from laser fields. The percentage of CH₃⁺ + X dissociation increased when the C–X bond was aligned with the laser field. Alignment also increased the branching ratio for H₂ elimination in CH₃NH₂⁺ and CH₃OH⁺ for isomerization in CH₃OH⁺.

INTRODUCTION

In simulations with Born–Oppenheimer molecular dynamics, we have shown that small molecular ions can absorb substantial amounts of energy from intense mid-IR laser pulses and undergo rapid reactions before intramolecular vibrational energy redistribution occurs.¹² In the present work, we examine the isomerization and fragmentation of CH₃NH₂⁺, CH₃OH⁺, and CH₃F⁺ by short intense 7 μm laser pulses. This work is motivated by recent studies of methanol cations by Yamanouchi and co-workers using pump–probe coincidence momentum imaging.³–¹⁰ A 40 fs, 800 nm pump pulse produced the monocation, and a probe pulse, delayed by 100–800 fs, ionized it to the dication. Coincidence imaging of specific fragmentations of the dication, CH₃OH²⁺ → CH₃⁺ + OH⁺ and CH₃OH⁺ → CH₃⁺ + H₂O⁺, showed that isomerization occurred during and shortly after the pulse.⁹,¹⁰

In prior work, we used ab initio classical trajectory calculations to investigate the dynamics of the methanol monocation on the ground-state potential energy surface in the presence of a strong laser field.¹¹,¹² Classical dynamics simulations showed that ground-state methanol cation gained only a few kcal/mol from an 800 nm laser field, suggesting that excited states and coupled nuclear–electron dynamics may be important for interactions with 800 nm laser pulses. By contrast, mid-IR laser fields interacted directly with the molecular vibrations of CH₃OH⁺, depositing enough energy to cause significant amounts of isomerization and dissociation on the ground-state surface.¹² Our simulations of CICO⁺, CF₃Br⁺, and C₆H₅I⁺ showed that intense mid-IR pulses were able to selectively enhance specific reaction channels for aligned molecules.¹² Therefore, in the present paper, we focus on mid-IR laser pulses and consider both randomly oriented and aligned molecules.

In the current study, we explore the effect of changes in potential energy surface on the reactions driven by the laser field. Like CH₃OH⁺, the reaction channels for CH₃NH₂⁺ and CH₃F⁺ include H elimination, H₂ loss, CH₃X → CHXH isomerization, and C–X dissociation. Differences in the barriers for these reactions range from 10 (H elimination) to over 50 kcal/mol (C–X dissociation). Born–Oppenheimer molecular dynamics have been used to model the isomerization and fragmentation of both randomly oriented and aligned CH₃X⁺ in short, intense laser pulses. As in earlier studies,¹¹,¹² the simulations used wavelengths of 7 μm and intensities of 8.8 × 10¹⁴ and 2.9 × 10¹⁴ W/cm² (field strengths of 0.05 and 0.07 au).

METHODS

Electronic structure calculations were carried out with the development version of the Gaussian series of programs.¹³ Field-free reaction energetics were calculated at the CAM-B3LYP/6-31G(d,p) and CBS-QB3 levels of theory.¹⁴,¹⁵ Molecular dynamics simulations in intense laser fields were carried out with the CAM-B3LYP/6-31G(d,p) level of theory. The amount of Hartree–Fock exchange in CAM-B3LYP increases from 19% at short-range to 65% at long-range (0.33
range parameter) and should be better than B3LYP at describing the long-range exchange behavior of the density distorted by the strong laser field.\textsuperscript{16} The interaction of the molecule with the laser field was calculated in the semiclassical dipole approximation.

$$\tilde{\mathbf{H}}(t) = \tilde{\mathbf{H}}_0(t) - \tilde{\mathbf{E}}(t)$$

$$\tilde{E}(t) = \tilde{z}(t) \sin(\omega t - \phi)$$  \hspace{1cm} (1)

\(\tilde{\mathbf{E}}(t)\) is the electric field component of the laser, and \(\tilde{z}(t)\) describes the shape of the pulse. The present study used a four-cycle linearly polarized trapezoid pulse

$$\tilde{z}(t) = \left(\frac{\alpha t}{2\pi}\right)E_{\text{max}} \text{ for } 0 \leq t \leq \frac{2\pi}{\omega}$$

$$\tilde{z}(t) = E_{\text{max}} \text{ for } \frac{2\pi}{\omega} \leq t \leq \frac{6\pi}{\omega}$$

$$\tilde{z}(t) = \left(4 - \frac{\alpha t}{2\pi}\right)E_{\text{max}} \text{ for } \frac{6\pi}{\omega} \leq t \leq \frac{8\pi}{\omega}$$  \hspace{1cm} (2)

or a cosine squared pulse

$$\tilde{z}(t) = E_{\text{max}} \cos\left(\frac{\alpha t - \pi}{2}\right) \text{ for } 0 \leq t \leq \frac{8\pi}{\omega}$$

$$\tilde{z}(t) = 0 \text{ otherwise}$$  \hspace{1cm} (3)

The 7 \(\mu\)m pulses had maximum field strengths, \(E_{\text{max}}\), of 0.05 and 0.07 au (intensities of 0.88 and 1.7 \(\times 10^{14}\) W/cm\(^2\), respectively). The direction of the laser field was chosen to be oriented randomly or aligned with the C–X bond axis.

Classical trajectories were integrated using our Hessian-based predictor–corrector algorithm.\textsuperscript{19} This method approximates the surface by a distance-weighted interpolant (DWI) using the first and second derivatives of the energy. The first derivative of the gradient with respect to the electric field was also included in the predictor and the corrector steps. The velocity Verlet method with \(\delta t = 0.0025\) fs was used to integrate both the predictor and corrector steps on the DWI surface. An overall step size of \(\Delta t = 0.25\) fs was used, and the Hessian was updated\textsuperscript{18,19} for 20 steps before being recalculated analytically. The starting structures had no rotational energy, and zero-point vibrational energy was added to the initial structures using classical sampling of the momentum.\textsuperscript{20} Approximately 100–200 trajectories were calculated for each set of starting conditions. The results of the trajectory calculations are listed in Table S1 of the Supporting Information. A few trajectories dissociated sequentially into multiple fragments; these were classified by the first dissociation event (see Table S1 footnote, Supporting Information). Some of the trajectories showed an unusually high gain in energy. This problem was traced to large charge oscillations when some bonds were stretched to more than 3 \(\AA\) within the laser pulse. Because the electronic structure was converged at each step of the trajectory integration rather than propagated, the charge on the fragments in some elongated bonds varied from plus to minus as the field changed the sign. These trajectories were discarded as artifacts of the Born–Oppenheimer molecular dynamics approach.

### RESULTS AND DISCUSSION

#### Energetics

The energetics for the fragmentation and isomerization of CH\(_3\)NH\(_2\)+, CH\(_3\)OH\(_+\), and CH\(_3\)F\(_+\) were calculated at the CAM-B3LYP/6-31G(d,p) and CBS-QB3 levels of theory and are shown in Figure 1. As in our earlier study of methanol cation,\textsuperscript{11} the DFT results agree relatively well with the more accurate calculations. The geometries and more detailed potential energy diagrams can be found in the Supporting Information. In all cases, the lowest-energy channel corresponds to C–H bond cleavage, and the CH\(_X\)+ product has C–X double bond character (C–N = 1.275, C–O = 1.246, and C–F = 1.233 Å at the CBS-QB3 level of theory). The C–H bond dissociation energies for CH\(_3\)OH and CH\(_3\)F are \(\sim 9\) kcal/mol smaller than those for CH\(_3\)NH\(_2\)+ at the CBS-QB3 level of theory. A similar trend of closely spaced energies for CH\(_3\)OH\(_+\) and CH\(_3\)F\(_+\) and higher energies for CH\(_3\)NH\(_2\)+ is observed for the H\(_2\) elimination reaction and the barrier for 1,2-hydrogen shift isomerization. The isomerization reaction is nearly thermoneutral for CH\(_3\)NH\(_2\)+ and CH\(_3\)HF\(_+\) but slightly exothermic for CH\(_3\)OH\(_+\). The cleavage of the C–X bond can occur before or after isomerization. In both cases, the trend in the dissociation energies is CH\(_3\)NH\(_2\)+ > CH\(_3\)OH\(_+\) > CH\(_3\)F\(_+\), which is opposite the ordering for the neutrals (83 kcal/mol for CH\(_3\)NH\(_2\), 91 kcal/mol for CH\(_3\)OH, and 110 kcal/mol for CH\(_3\)F at CBS-QB3). This can be understood in terms of orbital interactions. The C–X bonds in the cations dissociate heterolytically, CH\(_X\)+ \(\rightarrow\) CH\(_3\)+ + X and CH\(_3\)X\(_H\)+ \(\rightarrow\) CH\(_2\)+ + XH. The C–X bond in the cation is formed by interaction of an X lone pair with an empty carbon p orbital. The lone pair on F is lower in energy than O and interacts more weakly with the empty p on C, resulting in a C–F bond that is weaker than C–O. Similarly, the higher-energy N lone pair interacts more strongly with the carbon p orbital and forms a C–N bond that is stronger than the C–O bond.

#### Dynamics

To simulate the isomerization and fragmentation of CH\(_X\)+ by intense four-cycle 7 \(\mu\)m laser pulses, classical trajectories were calculated on the ground-state potential energy surface of the cation using the CAM-B3LYP/6-31G(d,p) level of theory. Simulations were carried out with trapezoidal-shaped laser pulses to maximize the interaction with the laser. For each field strength, approximately 200 trajectories were calculated for each molecule with the trapezoid pulse. Additional sets of 100 trajectories were computed with cosine squared pulses and a field strength of 0.07 au. Calculations were carried out for molecules oriented randomly in the laser field and for molecules with the C–X bond aligned with the laser polarization. On the basis of work with CICHO\(_+\), CF\(_6\)Br\(_+\), and C\(_6\)H\(_5\)I\(_2\)+,\textsuperscript{12} alignment of the C–X bond with the laser field should enhance C–X fragmentation and 1,2-hydrogen migration.

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**Figure 1.** Comparison of the low-energy fragmentation and isomerization channels (in kcal/mol) for CH\(_3\)NH\(_2\) (blue), CH\(_3\)OH (red), and CH\(_3\)F (green) calculated at the CBS-QB3 (bold) and CAM-B3LYP/6-31G(d,p) levels of theory.
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Table 1. Branching Ratios for the Reactive Trajectories in Percentages for CH₃X⁺ (X = NH₂, OH, and F)

<table>
<thead>
<tr>
<th>molecular species</th>
<th>orientation</th>
<th>field strength and pulse shape</th>
<th>average energy absorbed (kcal/mol)</th>
<th>fraction of trajectories reacting</th>
<th>CH₃X⁺ + H</th>
<th>CH₃⁺ + X</th>
<th>CH₃XH⁺</th>
<th>CH₃⁺ + HX</th>
<th>HCX⁺ + H₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃NH₂⁺</td>
<td>random</td>
<td>0.07 au, cosine sq</td>
<td>63.7</td>
<td>0.11</td>
<td>100.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.05 au, trapezoid</td>
<td>54.1</td>
<td>0.14</td>
<td>92.9</td>
<td>3.6</td>
<td>3.6</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>aligned</td>
<td>0.07 au, trapezoid</td>
<td>112.4</td>
<td>0.56</td>
<td>91.2</td>
<td>1.0</td>
<td>2.0</td>
<td>0.0</td>
<td>5.9°</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.05 au, trapezoid</td>
<td>112.0</td>
<td>0.59</td>
<td>84.8</td>
<td>1.7</td>
<td>5.9</td>
<td>0.0</td>
<td>7.6°</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.07 au, trapezoid</td>
<td>212.3</td>
<td>0.66</td>
<td>63.0</td>
<td>3.2</td>
<td>0.6</td>
<td>0.0</td>
<td>33.1°</td>
</tr>
<tr>
<td>CH₃OH⁺</td>
<td>random</td>
<td>0.07 au, cosine sq</td>
<td>34.5</td>
<td>0.40</td>
<td>76.9</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
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<tr>
<td></td>
<td></td>
<td>0.05 au, trapezoid</td>
<td>41.8</td>
<td>0.35</td>
<td>82.9</td>
<td>4.3</td>
<td>0.0</td>
<td>12.9°</td>
<td></td>
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<tr>
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<td>80.7</td>
<td>0.73</td>
<td>79.7</td>
<td>0.8</td>
<td>2.5</td>
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<td>0.05 au, trapezoid</td>
<td>75.5</td>
<td>0.72</td>
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<td>8.4</td>
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<tr>
<td></td>
<td></td>
<td>0.07 au, trapezoid</td>
<td>120.5</td>
<td>0.92</td>
<td>64.6</td>
<td>2.7</td>
<td>4.1</td>
<td>0.0</td>
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</tr>
<tr>
<td>CH₃F⁺</td>
<td>random</td>
<td>0.07 au, cosine sq</td>
<td>36.3</td>
<td>0.40</td>
<td>82.9</td>
<td>0.0</td>
<td>4.9</td>
<td>4.9</td>
<td>7.3°</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.05 au, trapezoid</td>
<td>33.3</td>
<td>0.34</td>
<td>75.8</td>
<td>1.5</td>
<td>7.6</td>
<td>0.0</td>
<td>15.2°</td>
</tr>
<tr>
<td></td>
<td>aligned</td>
<td>0.07 au, trapezoid</td>
<td>69.4</td>
<td>0.78</td>
<td>79.6</td>
<td>2.6</td>
<td>2.6</td>
<td>2.6</td>
<td>13.3°</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.05 au, trapezoid</td>
<td>58.0</td>
<td>0.69</td>
<td>72.5</td>
<td>4.4</td>
<td>7.2</td>
<td>0.7</td>
<td>15.2°</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.07 au, trapezoid</td>
<td>105.0</td>
<td>0.97</td>
<td>67.3</td>
<td>6.7</td>
<td>2.4</td>
<td>6.1</td>
<td>17.6°</td>
</tr>
</tbody>
</table>

*33.3% of those are CH₂NH⁺ + H₂. 31.4% of those are CH₂NH⁺ + H₂. 30% of those are CH₂O⁺ + H₂. 4.8% of those are CH₂O⁺ + H₂.*

The average amounts of energy gained from the laser pulse are listed in Table 1. A cosine squared pulse with a field strength of 0.07 au deposited approximately the same amount of energy as a trapezoid pulse with a field strength of 0.05 au. This is in accord with the fact that the integrated intensities of these two pulses are nearly equal. For each molecule, the percentage of reactive trajectories correlates very well with the average amount of energy deposited, as shown in Figure 2.

Figure 2. Percentage of reactive trajectories as a function of energy gained (in kcal/mol): (a) CH₃NH₂⁺ (blue diamonds, dotted—dashed line), (b) CH₃OH⁺ (red squares, dashed line), and (c) CH₃F⁺ (green triangles, dotted line).

Comparing the molecules, it is evident that CH₃NH₂⁺ requires a larger amount of energy than CH₃OH⁺ for the same degree of dissociation. This is in keeping with the larger barriers for CH₃NH₂⁺. Correspondingly, less energy is needed for CH₃F⁺ because it has lower barriers than CH₃OH⁺.

The distributions of energy gained by CH₃X⁺ (X = NH₂, OH, and F) from the trapezoidal laser pulse are shown in Figure 3. The spread in the energies is over 100 kcal/mol with somewhat longer tails toward higher energies. CH₃NH₂⁺ gained the most energy from the pulse, and CH₃F⁺ gained the least. Increasing the field strength from 0.05 to 0.07 au doubles the intensity (from 0.88 to 1.7 × 10¹⁴ W/cm²) and nearly doubles the amount of energy deposited.

Molecules with the C–X axis aligned with the laser polarization gained nearly twice as much energy from the laser pulse as molecules oriented randomly. This can be understood in terms of the vibrational spectra. The difference in intensity of the IR spectra of aligned and rotationally averaged CH₃X⁺ are shown in Figure 4 (individual spectra are available in the Supporting Information). When the C–X axis is aligned with the laser polarization, the intensities in the 1000–2000 cm⁻¹ range are significantly larger than those for the randomly oriented molecules. The vibrations in this region are primarily C–H bending modes. The distribution of frequencies of a four-cycle 7 μm trapezoidal pulse is centered around 1430 cm⁻¹ with a fwhm of ∼600 cm⁻¹. This covers the region where the aligned molecules absorb more strongly than those randomly oriented.

The results of trajectory calculations are summarized in Table 1. As expected from the higher barriers seen in Figure 1, the fraction of trajectories undergoing fragmentation and isomerization reactions for a given pulse shape and intensity is smallest for CH₃NH₂⁺. Most of the isomerizations and fragmentations occur after the pulse, but the fraction occurring within the pulse grows with increasing energy (reaching 20–25% for CH₃F⁺ with a field strength of 0.07 au; see Table S1, Supporting Information). Alignment of the C–X bond with the laser polarization increases the fraction of reactive trajectories as a consequence of the greater amount of energy gained from the pulse.

The branching ratio of various products as percentages for the reactive trajectories are listed in Table 1 and summarized graphically in Figure 5. Of the three low-energy channels, CH₃X⁺ → CH₂X⁺ + H is dominant in all cases, followed by H₂ elimination. Isomerization to CH₃XH⁺ is generally the next largest percentage. Although the 0.05 trapezoid pulse and the 0.07 au cosine squared pulse deposit similar amounts of energy, the latter produces less isomerization and CH₃⁺ + X dissociation. Compared to randomly oriented molecules, cations with the C–X bond aligned with the laser field have somewhat lower branching ratios for H dissociation and larger...
branching ratios for the other channels. Although the number of trajectories is small, alignment results in a factor of 3 increase in CH$_3$+ + X dissociation for several cases. For isomerization of CH$_3$OH$^+$ to CH$_2$OH$_2$+, the increase is nearly a factor of 2.

For CH$_3$NH$_2$+, little or no C−N bond breaking is seen, in keeping with the high dissociation energy. Only when the molecule is aligned with the field is a small amount of CH$_3$+ + NH$_2$ obtained. Isomerization and H$_2$ elimination are roughly comparable in magnitude. Even though the latter has a higher barrier, it is a looser transition state. The large percentage of H$_2$ elimination for aligned CH$_3$NH$_2$+ with 7 μm and a 0.07 field strength can be attributed to the large amount of energy gained from the pulse (212 kcal/mol).

The results for CH$_3$OH$^+$ in 800 nm and 7 μm laser fields have been reported previously.$^{11,12}$ Compared to CH$_3$NH$_2$+, CH$_3$OH$^+$ in a 7 μm laser field produces significantly more H$_2$ elimination than isomerization. This is in accord with the smaller difference in the two barrier heights in CH$_3$OH$^+$ compared to that in CH$_3$NH$_2$+. Alignment of the C−O bond with the laser field enhances the HCOH$^+$ + H$_2$ and CH$_2$OH$_2$ channels when compared to random orientation with the same laser parameters.

**Figure 3.** Histograms of the distribution of vibrational energy absorbed by CH$_3$X$^+$ (X = NH$_2$ (blue), OH (red), and F (green)) from a 95 fs, 7 μm trapezoidal laser pulse as a function of molecular orientation and maximum field strength: (a) random orientation, 0.05 au field, (b) C−X aligned, 0.05 au field, (c) random orientation, 0.07 au field, and (d) C−X aligned, 0.07 au field.
Of the three molecules, CH$_3$F$^+$ shows the most C$^−$X dissociation, as expected from the fact that it has the lowest C$^−$X bond dissociation energies. Only CH$_3$F$^+$ shows a significant amount of C$^−$X dissociation after isomerization, and this is highest when the C$^−$F bond is aligned with the field. However, alignment has little effect on isomerization.

**SUMMARY**

Energetics of the methylamine, methanol, and methyl fluoride cations were studied at the CAM-B3LYP/6-31G(d,p) and CBS-QB3 levels of theory. For all three molecules studied, isomerization, H elimination, and H$_2$ elimination were found to be low-energy reaction pathways.

The isomerization reaction was nearly thermoneutral for CH$_2$NH$_3^+$ and CH$_2$FH$^+$ but slightly exothermic for CH$_2$OH$^+$. Ab initio classical trajectory calculations were carried out with the CAM-B3LYP/6-31G(d,p) level of theory on the ground-state potential energy surface in the presence of a four-cycle, 95 fs, 7 μm laser pulse with maximum field strengths of 0.05 and 0.07 au (equivalently, intensities of 0.88 and 1.7 × 10$^{14}$ W/cm$^2$). The amount of energy absorbed was nearly doubled when the laser field was aligned along the C$^−$X axis and also when the field strength was increased from 0.05 to 0.07 au. The most abundant reaction path was CH$_2$X$^+$ + H (63%−100%), with HCX$^+$ + H$_2$ (0−33%) the second most abundant. Out of all of the trajectories studied, dissociation after isomerization was observed only in CH$_3$F$^+$ (0−6%). Alignment of the C$^−$X bond with the laser field increased the amount of CH$_3^+$ + X dissociation for all three molecules. Alignment also increased the branching ratio for isomerization in CH$_2$OH$^+$ and H$_2$ elimination in CH$_2$NH$_3^+$ and CH$_2$OH$^+$.

**ASSOCIATED CONTENT**

Supporting Information

Detailed potential energy diagrams for methylamine, methanol, and methyl fluoride cations, a summary of trajectory data,
individual IR spectra for the three monocations aligned with the laser field and rotationally averaged, and structures and Cartesian coordinates for selected molecules. This material is available free of charge via the Internet at http://pubs.acs.org.

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The authors declare no competing financial interest.

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