# Controlling Chemical Reactions by Short, Intense Mid-Infrared Laser Pulses: Comparison of Linear and Circularly Polarized Light in Simulations of ClCHO+ Fragmentation

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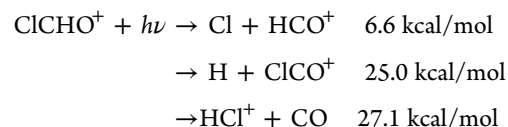
S **Supporting Information**

ABSTRACT: Enhanced mode selective fragmentation of oriented $ClCHO^+ \rightarrow Cl + HCO^+$, $H + ClCO^+$, $HCl^+ + CO$ with linear polarized intense mid-IR pulses was demonstrated in our previous computational study (*J. Phys. Chem. Lett.* **2012**, 3, 2541). Simulations of angle-dependent strong field ionization of ClCHO indicate the ionization rate in the molecular plane is nearly twice as large as perpendicular to the plane, suggesting a degree of planar alignment can be obtained experimentally for $ClCHO^+$, starting from neutral molecules. Classical trajectory calculations with a 4 cycle 7 μm laser pulse (peak intensity of 1.26×10^{14} W/cm^2) show that circularly polarized light with the electric field in the plane of the molecule deposits more energy and yields larger branching ratios for higher energy fragmentation channels than linearly polarized light with the same maximum field strength. These results suggest circularly polarized mid-IR pulses can not only achieve control on reactions but also provide an experimentally accessible implementation.
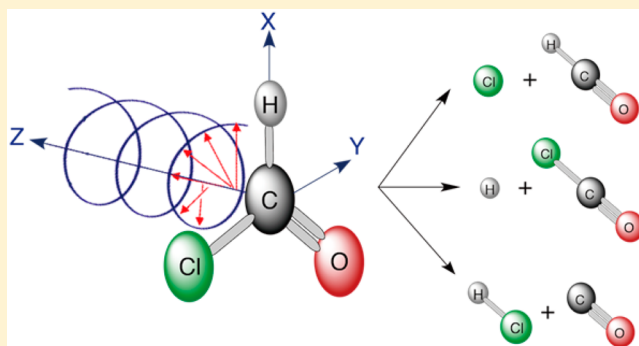
INTRODUCTION

Tunable mid-IR light can deposit energy efficiently into selected vibrational modes with the potential of achieving mode-selective reactions that are otherwise energetically disfavored. However, this resonant excitation and consequent reactivity is easily defeated by intramolecular vibrational redistribution (IVR) unless sufficient energy can be absorbed quickly and reaction occurs more rapidly than IVR.[1,2] This requires very short, intense IR pulses. In previous studies,[3,4] we used Born–Oppenheimer molecular dynamics (BOMD) to simulate selective reaction acceleration for orientated molecules by linearly polarized mid-IR pulse for $ClCHO^+$, CF_3Br^+, and $C_6H_5I^{2+}$. While technically possible, the prerequisite of three-dimensional (3D) molecular orientation is still very challenging. Therefore, a more experimentally accessible approach is needed. Recently, electron dynamics driven by intense elliptically polarized laser field has attracted considerable attention because such dynamics revealed intimate correlation among electron, laser electric field, and ionic cores.[5,6] However, whether elliptically polarized light could afford similar degrees of control over chemical reactions remains unexplored. In the present work, we examine the fragmentation of $ClCHO^+$ by circularly polarized light and compare the results to our previous study with linearly polarized light. We show that the answer to the aforementioned question is positive and also chemical control driven by circularly polarized light provides a real opportunity for experimental implementation.

There are three low energy channels for the dissociation of $ClCHO^+$. At the B3LYP/6-311G(d,p) level of theory, the dissociation energies are

$$ClCHO^+ + h\nu \rightarrow Cl + HCO^+ \quad 6.6 \text{ kcal/mol}$$
$$\rightarrow H + ClCO^+ \quad 25.0 \text{ kcal/mol}$$
$$\rightarrow HCl^+ + CO \quad 27.1 \text{ kcal/mol}$$

Classical trajectory calculations on the ground state Born–Oppenheimer potential energy surface showed that when the initial kinetic energy is distributed statistically or when the molecule is oriented randomly in a laser field the Cl dissociation is dominant.[3] However, when a linearly polarized 7 μm laser pulse with a peak intensity of 2.9×10^{14} W/cm^2 is aligned in the plane of the molecule, the high energy channels can be greatly enhanced. In particular, when the polarization direction is approximately parallel or antiparallel to the C–H bond, H dissociation increases by a factor of 3 over random orientation, and when the direction is perpendicular to the C–H bond and in the plane of the molecule the yield of HCl^+ is increased by a factor of 10. In the present study, we examine whether linearly polarized light can be used to generate the cation with a degree of alignment and explore dissociation by

Scheme 1. Coordinate System for the Simulation of Circularly Polarized Light Propagating Along the z-Axis Interacting with ClCHO$^+$ in the $x-y$ Plane Oriented so that the C−H Bond Is Along the x-Axis[a]
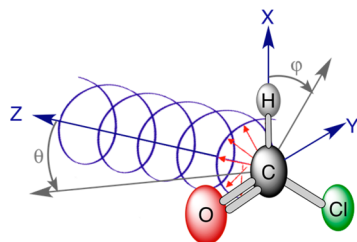
[a]θ is the polar angle with the z-axis and ϕ is the in-plane angle with the C−H bond.

circularly polarized light aligned so that the electric field vector rotates in the plane of the molecule. The coordinate system for the simulation is shown in Scheme 1. We start by using time-dependent configuration interaction calculations of the angular dependence of ionization to see if the cation can be prepared with some degree of alignment with linearly polarized light. Molecular dynamics simulations for the fragmentation of aligned ClCHO$^+$ are then carried out with circularly polarized light using a 4 cycle 7 μm pulse with a peak intensity of 1.26×10^{14} W/cm^2 (this deposits an amount of energy similar to linearly polarized light with an intensity of 2.9×10^{14} W/cm^2). The branching ratios and the distributions of the energies and angular momenta are compared for linearly and circularly polarized light.

■ METHOD

The angular dependence of ionization of neutral ClCHO was simulated by time-dependent configuration interaction calculations with a complex absorbing potential[7−10]

$$i\frac{\partial}{\partial t}\Psi_{el}(t) = [\hat{H}_{el} - \vec{\hat{\mu}}\cdot\vec{E}(t) - i\hat{V}^{absorb}]\Psi_{el}(t) \quad \Psi_{el}(t) = \sum_{i=0} C_i(t)|\Psi_i\rangle$$

(1)

where $\hat{H}_{el}$ is the field-free electronic Hamiltonian. The electron-light interaction is treated in the semiclassical dipole approximation, where $\vec{\hat{\mu}}$ is the dipole operator and $\vec{E}$ is electric-field component of the laser pulse. The absorbing potential used to model ionization, $-i\hat{V}^{absorb}$ is constructed from a set of overlapping spherical potentials around each atom. Each spherical

potential has a quadratic rise starting at 3.5 times the van der Waals radius R_{vdw} and a quadratic turnover to constant value of 10 hartree at approximately $R_{vdw} + 7$ Å. The time-dependent wave function is constructed from the field-free Hartree−Fock ground state and all singly excited configurations. The computations employed the aug-cc-pVTZ basis set[11,12] plus a large set of diffuse functions for a total of 289 basis functions and 2278 singly excited states. The time-dependent coefficients were propagated using a Trotter factorization of the exponential of the Hamiltonian. A 4 cycle linear polarized 7 μm sine-squared pulse with a maximum field strength of 0.06 au (corresponding to a peak intensity of 1.26×10^{14} W/cm^2) was used for the simulation of the ionization. The ionization yield was taken as the loss of norm of the wave function and was plotted as a function of the polarization direction of the pulse. Details of the procedure and validation of the methodology are described in a series of earlier papers.[7−10]

Dissociation was simulated by classical trajectory calculations on the ground state Born−Oppenheimer surface for aligned formyl chloride cations in the time varying electric field of laser pulse. The laser field was a 4 cycle 7 μm trapezoidal pulse (95 fs full width). This corresponds to 1430 cm^{-1} and a width of ca. 300 cm^{-1} and should interact strongly with a range of molecular vibrations. For circularly polarized light, the propagation direction was perpendicular to the plane of the molecule with the electric field rotating in the plane of the

Table 1. Branching Ratios for the Dissociation of ClCHO$^+$ Interacting with Circular and Linear Polarized Laser Pulses

polarization	field strength (au)	branching ratio		
		Cl + HCO$^+$	H + ClCO$^+$	HCl$^+$ + CO
field-free[a]	0	71%	18%	8%
field-free[b]	0	55%	24%	21%
left circular[c]	0.06	30%	47%	23%
right circular[d]	0.06	29%	52%	19%
linear (0−360° averaged)[e]	0.06	81%	15%	4%
linear (0−360° averaged)[f]	0.09	57%	22%	21%

[a]One hundred trajectories with 37.8 kcal/mol initial vibrational energy[3]; ca. 3% did not dissociate. [b]Three hundred trajectories with 54.0 kcal/mol initial vibrational energy[3]; ca. 2% did not dissociate. [c]Eight hundred trajectories; ca. 5% did not dissociate. [d]Eight hundred trajectories; ca. 4% did not dissociate. [e]Forty-eight hundred trajectories; ca. 41% did not dissociate. [f]Sixteen hundred trajectories; ca. 12% did not dissociate.
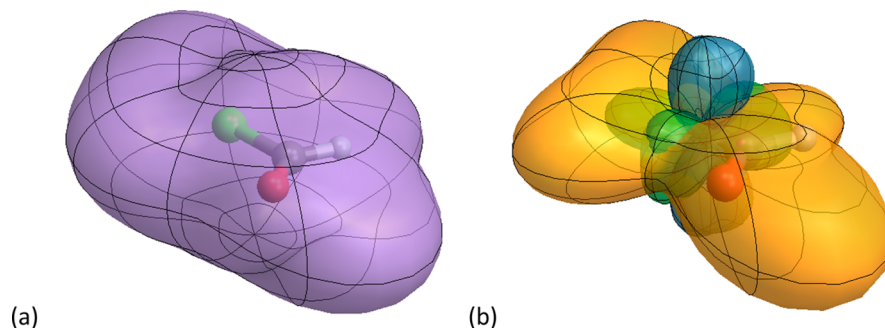

Figure 1. Angular dependence of (a) the total yield for the ionization of ClCHO as a function of the polarization direction and (b) the contributions of the HOMO (yellow), HOMO-1 (blue), and HOMO-2 (green) to the total ionization yield. The radial distance of the surface is proportional to the ionization yield for the corresponding polarization direction of a 4 cycle 7 μm linearly polarized sine-squared laser pulse with a maximum field strength of 0.06 au.

molecule with a maximum field strength of 0.06 au. For linearly polarized light, the polarization direction was in the plane of the molecule and the direction was varied from $\phi = 0-360°$ in steps of 30° with a maximum field strength of 0.06 au and steps of 90° with a maximum field strength of 0.09 au. Trajectories were integrated for a total of 400 fs. The B3LYP/6-311G(d,p) level of theory is a suitable compromise between accuracy of the potential energy surface and efficiency in the trajectory calculations. Molecular dynamics calculations were carried out with the development version of the Gaussian series of programs[13] and the PCvelV integrator[14] with a step size of 0.25 fs and Hessian updating[15,16] for 20 steps before recalculation. The starting structures had no rotational energy; zero-point vibrational energy was added to the initial structures using orthant sampling

of the momentum.[17] Trajectories that gained large amounts of energy due to unphysically large charge oscillations within a single laser cycle were discarded as artifacts of the Born–Oppenheimer approximation. Trajectories were classified into specific channels (Cl + HCO$^+$, H + ClCO$^+$, HCl$^+$ + CO, no reaction) based on bond lengths (details are given in the Supporting Information).

■ RESULTS AND DISCUSSION

The angular dependence of the ionization yield for ClCHO is shown in Figure 1a for a 7 μm linearly polarized laser pulse with a maximum field strength of 0.06 au (1.26×10^{14} W/cm^2). The ionization yield is about 80% larger for polarization directions in the plane of the molecule than for perpendicular to the

Table 2. Average Total Energy Absorbed by ClCHO$^+$ Interacting with Circular and Linear Polarized Laser Pulses

polarization[a]	field strength (au)	total energy(kcal/mol)			
		all channels	Cl + HCO$^+$	H + ClCO$^+$	HCl$^+$ + CO
left circular	0.06	89.3 ± 40.7	59.1 ± 25.1	94.4 ± 35.3	119.2 ± 41.0
right circular	0.06	99.7 ± 54.9	59.4 ± 28.5	123.7 ± 59.9	95.1 ± 26.1
linear (0–360° averaged)	0.06	38.4 ± 17.2	33.8 ± 12.2	57.5 ± 20.2	59.1 ± 24.9
linear (0–360° averaged)	0.09	86.1 ± 44.7	65.8 ± 28.2	112.6 ± 62.9	106.9 ± 35.1

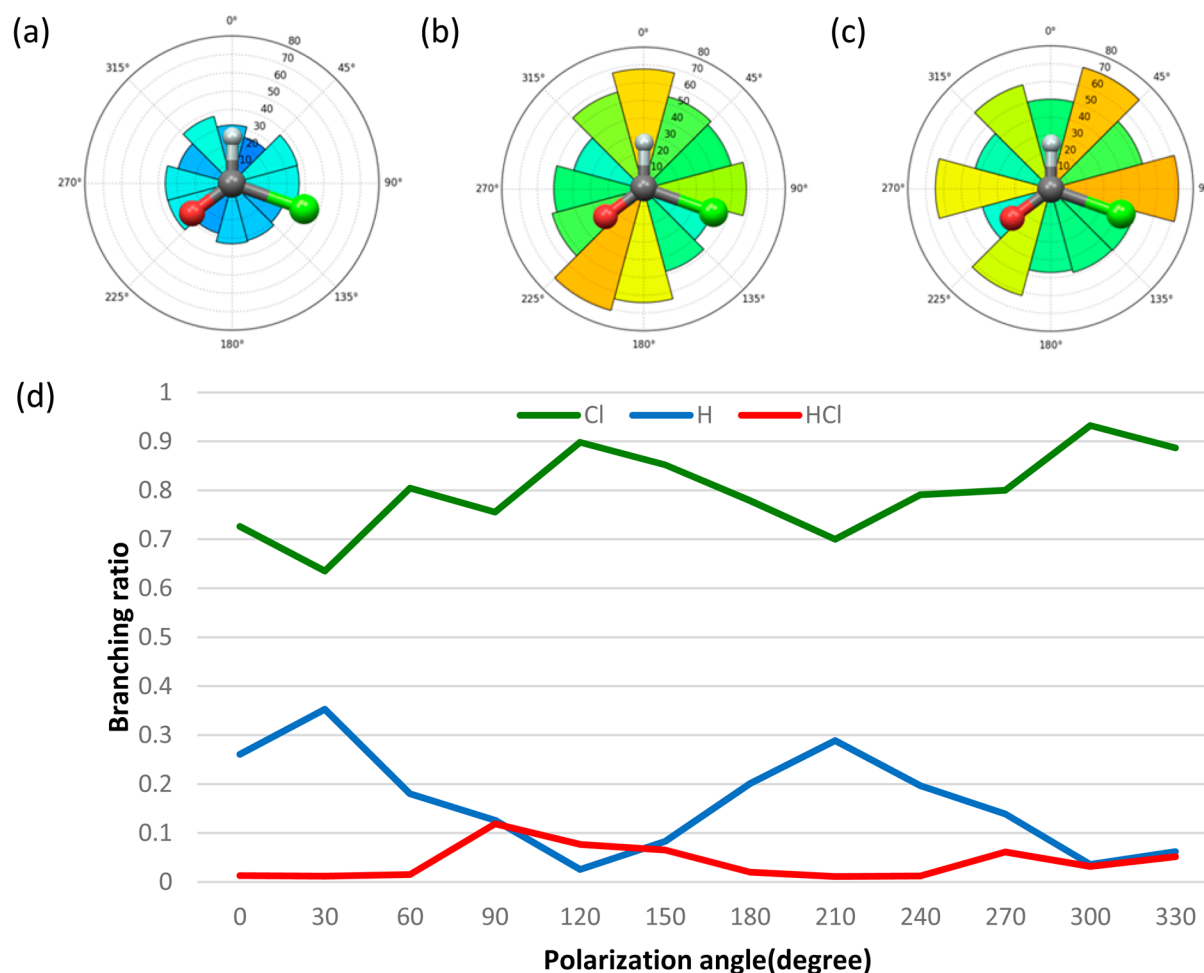[a]See footnotes of Table 1 for trajectory details.

Figure 2. Energy deposited as a function of the in-plane angle ϕ of the direction of linearly polarized light with a field strength of 0.06 au for (a) Cl + CHO$^+$, (b) H + ClCO$^+$, and (c) HCl$^+$ + CO; (d) branching ratio as a function of the in-plane angle ϕ of the direction of linearly polarized light with a field strength of 0.06 au.
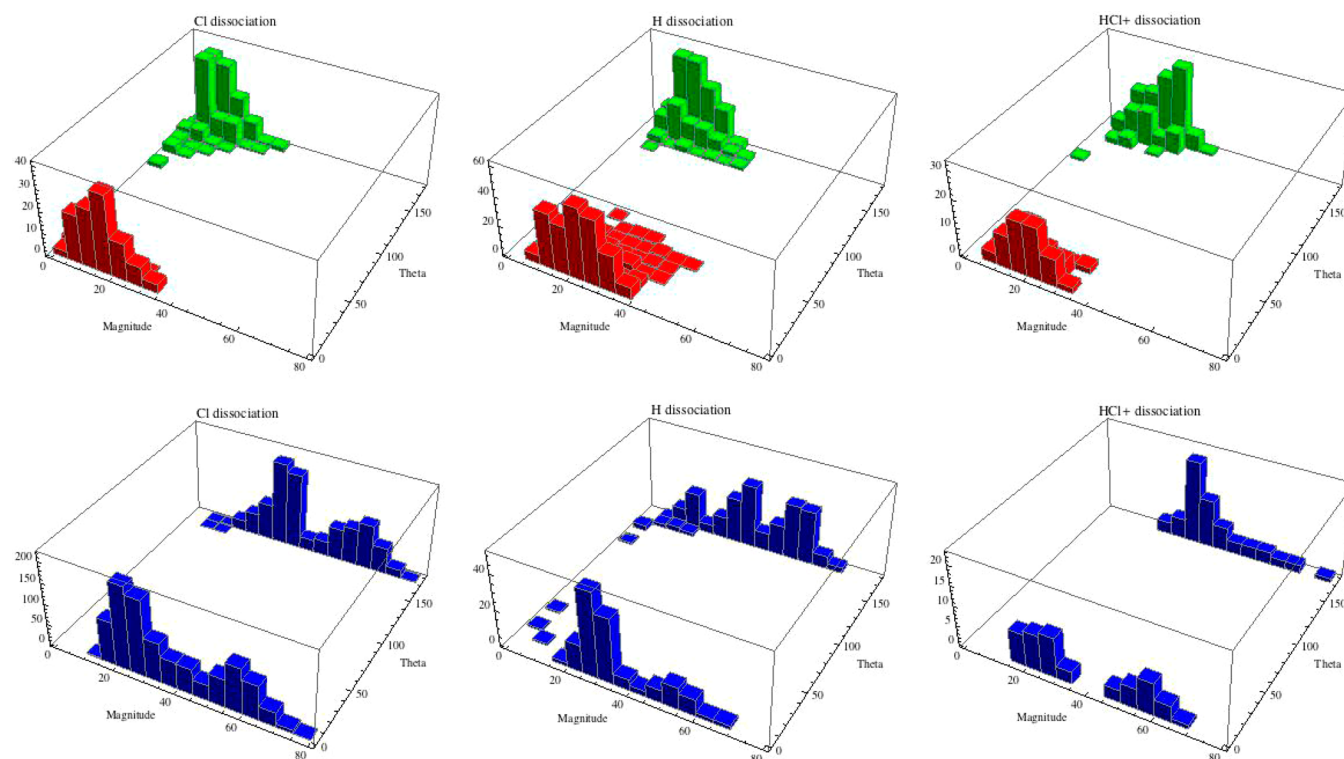
Figure 3. Magnitude and direction of the total angular momentum for the Cl + HCO$^+$, H + ClCO$^+$, and HCl$^+$ + CO channels with 0.06 field strength for left circularly polarized light (top row, green), right circularly polarized light (top row, red) and linearly polarized light averaged over $\phi = 0{-}360°$ (bottom row, blue).

plane. Interestingly, for in-plane directions the yield is about 65% greater when the polarization is aligned with the C−Cl bond compared to perpendicular to the bond. Therefore, ionization with linearly polarized light should result in appreciable alignment of the cation. This also suggests that a certain degree of planar alignment of the ions might be achieved via ionization using circularly polarized light with the electric field rotating in the plane of the molecule. Population analysis of the wave function shows that the cation is formed primarily by removal of an electron from the highest occupied molecular orbital (HOMO), an in-plane Cl lone pair orbital) as shown in Figure 1b. Some ionization from HOMO-1 (π-type Cl lone pair orbital) and HOMO-2 (the other in-plane Cl lone pair orbital) can also be seen.

The dissociation of ClCHO$^+$ was simulated by Born−Oppenheimer molecular dynamics. Approximately 65% of the ionization in the molecular plane comes from the HOMO and yields the cation in its ground state. Depending on their lifetimes, excited states of the cation could also contribute to the dissociation, but this is beyond the scope of the present study. Dissociation on the ground-state potential energy surface induced by linear and circularly polarized, intense mid-IR laser pulses can be compared with simulations of field-free fragmentation of activated ClCHO$^+$ that has enough initial vibrational energy to easily overcome the dissociation barriers for the three channels of interest.[3] Our previous study showed that in the field-free case the Cl channel was favored at lower initial energies and, as expected, the fraction of the higher energy H and HCl$^+$ channels increased for greater initial energies (see Table 1). Dissociation of unactivated ClCHO$^+$ by circular polarized pulses with a maximum field strength of 0.06 au yields more H + ClCO$^+$ and less Cl + HCO$^+$ than the

activated field-free cases. The branching ratios for right and left circularly polarized light are similar but not identical. The standard deviation for the branching ratios is 2−3% as estimating from the statistical uncertainty of $\sqrt{N}$. Thus, the difference in the branching ratios between right and left circularly polarized light may not be statistically significant. The results for circularly polarized pulses with a maximum field strength of 0.06 au can be compared to linearly polarized pulses averaged over $\phi = 0{-}360°$. The yield of H and HCl$^+$ is much less for linear polarized light than for circularly polarized light with the same maximum field strength. The field strength for the linear polarized pulses must be raised from 0.06 to 0.09 au to obtain a comparable fraction of higher energy products. Thus, for a given maximum field strength, circularly polarized light is more effective than linearly polarized light in producing higher energy fragmentation products.

As indicated by the simulations of activated ClCHO$^+$ in the field free case, the branching ratios for the products should depend on the amount of internal energy. Table 2 lists the average total energy absorbed by ClCHO$^+$ interacting with circularly and linearly polarized laser pulses. Circularly polarized light deposits approximately twice as much energy as linearly polarized light with the same maximum field strength. This is because a circularly polarized light pulse can be decomposed into two perpendicular linearly polarized pulses with the same intensity and a phase difference of ±90°. Because the energy of a classical wave is proportional to the amplitude squared, linearly polarized light with a field strength of 0.09 au deposits approximately twice as much energy as with a field strength of 0.06 au. The increased energy deposited by linearly polarized light with a field strength of 0.09 au brings the branching ratio closer to that of circularly polarized light with a field strength of 0.06 au (see Table 1).
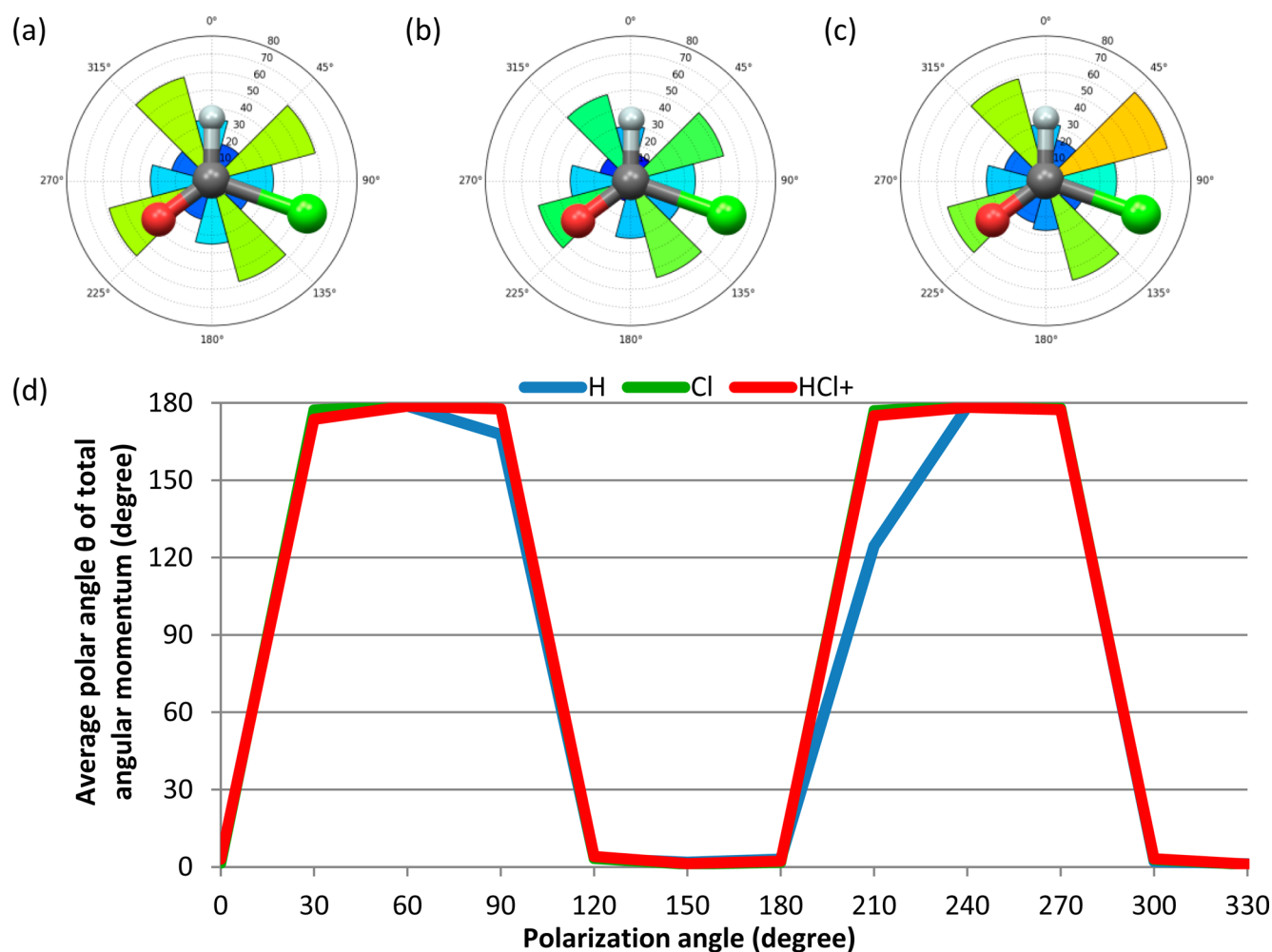
Figure 4. Total angular momentum of the products as a function of the in-plane angle ϕ of the direction of linearly polarized light with a field strength of 0.06 au for (a) Cl + CHO$^+$, (b) H + ClCO$^+$, and (c) HCl$^+$ + CO; (d) polar angle θ for the total angular momentum as a function of the in-plane angle ϕ of the direction of linearly polarized light with a field strength of 0.06 au.

The amount of energy deposited by linearly polarized light depends on the reaction channel (Table 2) and the orientation of the field (Figure 2). For both linear and circularly polarized light, the products of the lower energy Cl + HCO$^+$ channel gain only about one-half to two-thirds as much energy as the products of the higher energy H + ClCO$^+$ and HCl$^+$ + CO channels. For the H + ClCO$^+$ channel, the most energy is absorbed when the polarization is nearly parallel with the C−H bond (Figure 2b). Similarly for the HCl$^+$ + CO channel, the highest amount of energy is absorbed for polarization directions between the C−H and C−Cl bonds (Figure 2c). The branching ratios shown in Figure 2d are in qualitative agreement with the angular dependence of the energy absorbed. The yield is greatest for the low energy Cl + HCO$^+$ channel, which has a broad maximum when the polarization is roughly parallel to the C−Cl bond. There is a decrease in the Cl yield (and a corresponding sharp rise in the number of unreactive trajectories) when the field is perpendicular to the C−Cl bond. This indicates that the coupling of between the laser field and the molecule is strong when the polarization direction is aligned with the C−Cl bond but weaker when the direction is perpendicular to the C−Cl bond. The H + ClCO$^+$ channel has a broad maximum when the field is roughly parallel or antiparallel to the C−H bond, leading to an enhancement of about 2 compared to the average over ϕ = 0−360°. Similarly,

the HCl$^+$ + CO channel has a broad maximum when the field is approximately perpendicular to the C−H bond, yielding an enhancement of 2−3. This angular dependence of the branching ratios for linearly polarized light is more pronounced at higher field strengths. In a previous paper, we found an order of magnitude increase in the HCl$^+$ branching ratio when a field of 0.09 au was oriented perpendicular to the C−H bond.

The distributions of product total angular momenta are shown in Figure 3. In the simulations, the electric field vectors for both linearly and circularly polarized laser pulses are in the plane of the molecule. Consequently, the dissociating fragments remain close to the molecular plane and the angular momentum vectors are mainly perpendicular to the plane ($\theta \approx 0°$ and 180°). Similar to the distribution of the energy absorbed, the magnitudes of the angular momenta cover a broad range. Except for very small magnitudes of the angular momentum, all of the dissociating trajectories for right circularly polarized light are close to $\theta = 0°$ and those for left circularly polarized light are close to $\theta = 180°$. For linearly polarized light, the magnitudes of the angular momenta are larger and both directions $\theta \approx 0°$ and $\theta \approx 180°$ are found, depending on the direction of the polarization.

The angular momentum of the products results from the interaction of the electric field of the light with the permanent dipole and polarizability of the molecule. For ClCO$^+$ in a field
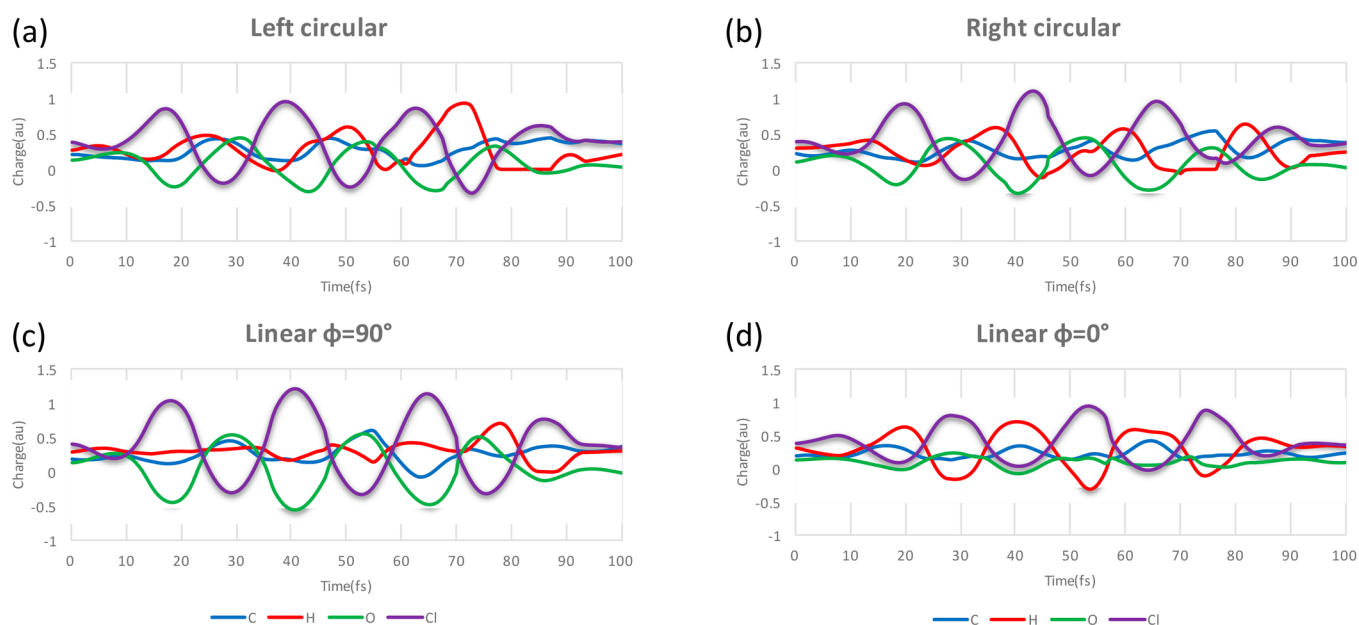
Figure 5. Mulliken charges as a function of time during the pulse for (a) left circularly polarized light, (b) right circularly polarized light, (c) linearly polarized light with $\phi = 90°$ (aligned with the CH bond), and (d) linearly polarized light with $\phi = 0°$ (aligned perpendicular to the CH bond) (0.06 au field strength for circular polarized light and 0.09 au field strength for linear polarized light).

of 0.06 au, these terms account for ca. 90% of the interaction energy. The potential energy of a polarizable homonuclear diatomic in an electric field is $V(\phi) = -(1/2)\varepsilon^2(\alpha_{\parallel} \cos^2 \phi + \alpha_{\perp} \sin^2 \phi)$ and the torque is $\tau = -dV/d\phi$, where $\alpha_{\parallel} > \alpha_{\perp}$ are the polarizabilities parallel and perpendicular to the bond. The diatomic system experiences a maximum positive torque for $\phi = -45°$, $+135°$ and a maximum negative torque for $\phi = +45°$, $-135°$. Figure 4 shows total angular momentum of the products as a function of the direction of linearly polarized light. The major axis of the polarizability tensor for ClCHO$^+$ is along the C−Cl bond. The magnitudes of the total angular momenta have maxima at approximately $\pm45°$ and $\pm135°$ to the C−Cl bond (Figure 4a−c), and the polar angle θ of the angular momentum alternates between $0°$ and $180°$ as the field is rotated (Figure 4d), analogous to the behavior of a simple polarizable diatomic molecule in a strong field.

For low field strengths, the coupling between light and molecular vibrations depends on the change in the dipole moment with respect to the geometric parameters, or equivalently, the change in the forces on the atoms with the applied electric field ($-d\mu/dR = dg/d\varepsilon = d^2E/dRd\varepsilon$). For higher field strengths, the response of the molecule to the external field can dominate the interaction. Figure 5 shows the Mulliken charge distribution as a function of time for ClCHO$^+$ in right and left circular polarized pulses and for two orientations of a linearly polarized pulse. The largest oscillations in charge are for the chlorine and for the oxygen. For linearly polarized light at $\phi = 0°$ and $90°$, oscillations in chlorine and oxygen are nearly equal and opposite. For circularly polarized light, the charges change most when the rotating field is aligned with the bond. As a result, the oscillation of the charge on the chlorine either leads or lags behind the oscillation of the charge on the oxygen, depending on direction of rotation of the electric field of the circularly polarized light. This phase difference may lead to the difference in the total angular momentum seen in the dissociation of ClCHO$^+$ induced by right and left circularly polarized light.

■ SUMMARY

The present simulations for ClCHO$^+$ show that circularly polarized light is more effective than linearly polarized light of the same peak intensity in depositing energy and causing fragmentation. This results in a higher yield of high energy products for circularly polarized light. The branching ratios and energy absorbed are similar for right and left circularly polarized light, but the total angular momentum vectors have opposite directions. Even though linearly polarized light deposits less total energy, it yields higher values of the total angular momentum than circularly polarized light. At these high field strengths, the coupling with the light is dominated by the polarizability of the molecule. For linearly polarized light, this can be seen from the angular dependence of the increase in energy and angular momentum and from the charge fluctuations. Our calculation also suggests the possibility of implementing such an experiment with a single laser achieving ionization of neutral and control of ion fragmentation at the same time.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpca.5b12327.

> Trajectory classification method, sample results for alternative laser field conditions, and decomposition of the total angular momentum into fragment contributions. (PDF)

■ AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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