A Reaction Accelerator: Mid-infrared Strong Field Dissociation Yields Mode-Selective Chemistry

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ⓢ *Supporting Information*

ABSTRACT: Mode-selective chemistry has been a dream of chemists since the advent of the laser in the 1970s. Despite intense effort, this goal has remained elusive due to efficient energy randomization in polyatomic molecules. Using ab initio molecular dynamics calculations, we show that the interaction of molecules with intense, ultrashort mid-infrared laser pulses can accelerate and promote reactions that are energetically and entropically disfavored, owing to efficient kinetic energy pumping into the corresponding vibrational mode(s) by the laser field. In a test case of formyl chloride ion photodissociation, the reactions are ultimately complete under field-free conditions within 500 fs after the laser pulse, which effectively overcomes competition from intramolecular vibrational energy redistribution (IVR). The approach is quite general and experimentally accessible using currently available technology.

SECTION: Spectroscopy, Photochemistry, and Excited States
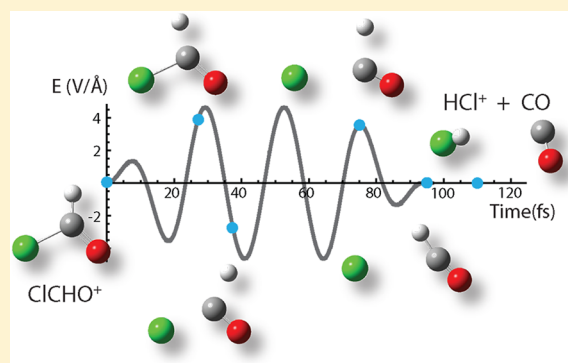
On a single electronic potential energy surface of a molecule, e.g., the ground state, large-amplitude and concerted motions are required for chemical transformation. This large amplitude motion allows significant nuclear rearrangement, and concerted motions among a few degrees of freedom are necessary to effect the passage through the transition state region that connects the reactant and products.[1] Under general conditions, both requirements are satisfied by the incoherent motions of vibration and rotation of an energized molecule. Therefore, most reactions are stochastic in nature. Mode-specific chemistry, as envisioned 30 years ago, attempted to exploit the fact that some degrees of freedom are more closely coupled to the reaction coordinate: by locally exciting these modes with tunable lasers to provide such large amplitude motions, one hoped to exert control over a reaction.[2,3] Unfortunately, this dream of mode-specific chemistry was foiled for polyatomic molecules due to rapid intramolecular vibrational energy redistribution (IVR):[4,5] the scrambling of the energy among all degrees of freedom, which has a typical time scale of a few picoseconds. For reactions with similar or longer reaction time, IVR generally leads to the breaking of the weakest bond and thus no mode-specificity. In the past decades, while a few examples were shown to have successfully overcome IVR,[6–8] a general approach has not emerged. In order to defeat IVR, two conditions are critical: (1) ultrafast, mode-specific excitation must be achieved, and (2) ultrashort reaction times for dissociation or isomerization (<1 ps) must prevail. Both requirements can be achieved if a large amount of kinetic energy can be directly deposited into specific vibrational mode(s) during an ultrashort pulse. The high kinetic energy forces the reaction to proceed in a "prompt" fashion and thus accelerate the reaction. This is indeed the key to mode-specific reaction in many systems, but so far it has not been generally achieved. Previously, electronic excitation by ultrafast lasers has been used successfully to accomplish this in some cases, but this method is limited by the details of the vibronic coupling and the small number of vibrational modes accessible from the Franck–Condon region.[6] Vibration excitation in the ground electronic state has been shown to alleviate such limits and allows access to larger regions of the excited potential energy surface,[7,9] even though such an excitation scheme does not warrant an ultrashort reaction time. Adiabatic passage based methods (e.g., Raman chirped pulse adiabatic passage (RCAP)[10] and stimulated Raman adiabatic passage (STIR-AP)[11]) are very efficient for population transfer. However, these approaches require slow chirping of the frequency, and thus their time scales are limited to ~picoseconds, and hence defeated by IVR.

In this Letter, we demonstrate theoretically that interaction with an intense ultrashort *mid-infrared* laser pulse can pump a large amount of kinetic energy into selected vibrational modes and thus accelerate dissociation along a chosen pathway. We show in the particular case of formyl chloride cation that HCl⁺ elimination is enhanced dramatically compared to the energetically favored simple bond fission reactions by exciting two vibrational modes that are closely coupled to the desired
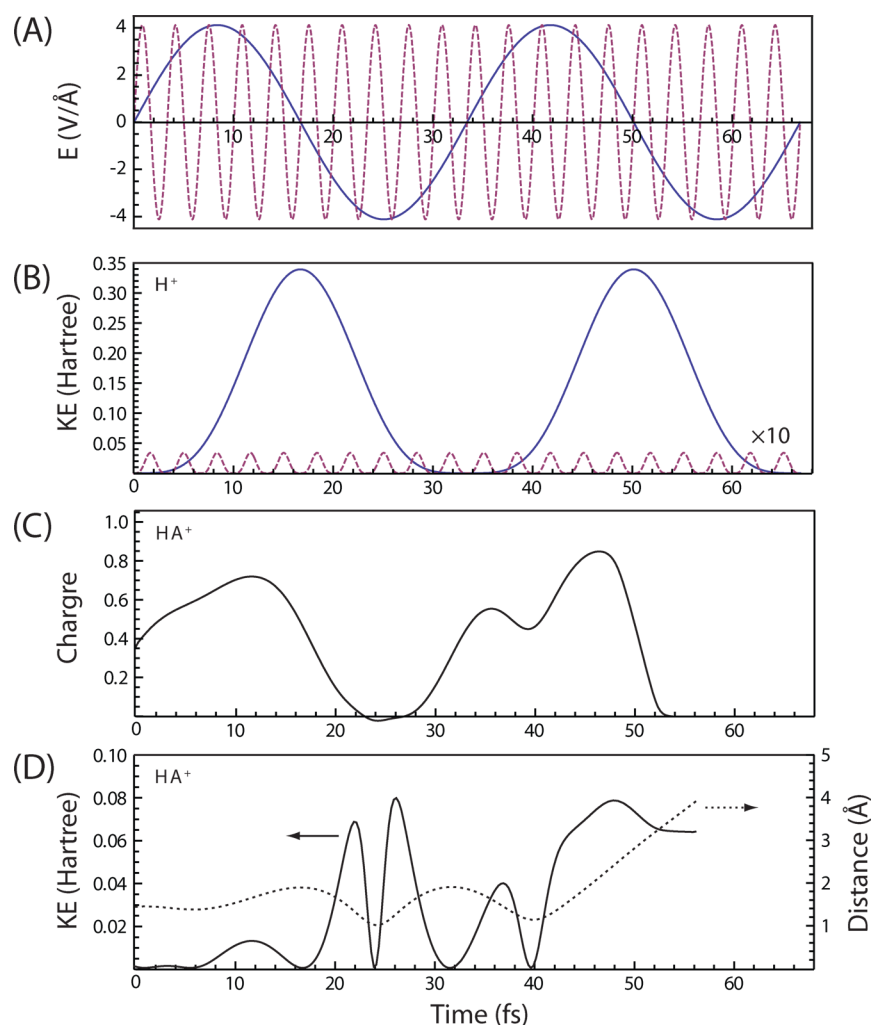
Figure 1. Pumping kinetic energy into atoms by a strong laser field. (A) The oscillating electric field of 800 nm and 10 μm laser pulses with the same laser intensity (2.3×10^{14} W/cm^2). (B) The kinetic energy of a free proton in the fields shown in (A). Note in the end of each full cycle, the kinetic energy goes to zero due to the cancellation between the positive and negative part of the pulses. The kinetic energy is more than 2 orders of magnitude higher in the 10 μm laser field than that in the 800 nm laser field. (C) An illustration of the charge evolution of a nonfree hydrogen atom (i.e., in a molecule HA$^+$) in a 10 μm laser field. (D) The kinetic energy of the nonfree hydrogen atom in the laser field (solid line) and the temporal evolution of the distance between the hydrogen and its cofragment(s), suggesting a dissociation event (dashed line).

reaction coordinate. We achieve this by using an ultrashort mid-IR laser pulse while at the same time aligning the molecules at specific angles with respect to the laser polarization. Another requirement is that the laser intensity is in the range of 10^{14} W/cm^2, which is 5 orders of magnitude higher than that in conventional infrared multiphoton dissociation (IRMPD) and 2 orders of magnitude higher than that of previous experiments using mid-IR lasers to excite vibrational motion in molecules.[8] Molecular cations are found to be generally suitable to apply such method due to their small ionization probability in a strong field. With the combination of ultrashort laser pulses and spatially aligned/orientated molecules, our proposed method achieves two long-standing goals of chemical control experiments: rational spatial and temporal control of a chemical reaction at the atomic level and in the femtosecond time domain.

A strong laser field can distort the Coulomb potential significantly when the laser electric field is comparable to that between electrons and nuclei. Such distortion can lead to tunneling or over-the-barrier ionization due to the suppressed Coulombic barrier on one side of the nucleus.[12,13] In molecules,

the strong electric field polarizes the charge distribution and exerts forces on constituent ions and thus distorts the molecular potential. A strong nonresonant coupling between two electronic states with the same asymptotic charge distribution (charge resonance states) can even completely suppress the molecular potential of the adiabatic ground state.[14,15] While a free electron/ion cannot gain energy from an oscillating field (Figure 1A,B), constituent ions in a molecule can easily achieve this because they carry different charges in the positive and negative part of the laser cycle and thus break the symmetry (Figure 1C,D). The average kinetic energy (i.e., the ponderomotive potential) that a charged particle can gain from the laser field is linearly proportional to the laser intensity and quadratically proportional to the driving laser wavelength. Therefore, with the same laser intensity, long wavelength driving lasers have a huge advantage over the widely used Ti:Sapphire laser (800 nm) in depositing kinetic energy into molecular systems. As shown previously, using intense 10 μm CO$_2$ laser pulses, H$_2^+$, HCl$^+$, and HCO$^+$ were not only dissociated but the fragments gained several electron volts (eV) of kinetic energy.[14,16−18] Furthermore, the field-induced charge

oscillation (and thus kinetic energy gain) is strongly anisotropic due to the angle dependence of the coupling matrix:[14] it is strongest when the bond is along the laser polarization and weakest in a perpendicular geometry. This feature provides the desired mode selectivity when combined with molecular axial alignment or orientation.

The calculation method used in this study is ab initio molecular dynamics (AIMD) based on the Born–Oppenheimer approximation and classical mechanics. In this method, the field-dressed electronic wave functions are computed by density functional theory (DFT) within a basis expansion, and the nuclear motion is propagated classically. The approach is capable of modeling larger systems with good accuracy and has been successfully applied in a few systems in strong fields.[18−20] A recent modification of the Hessian based predictor-corrector method[18] has significantly improved the time efficiency of the molecular dynamics simulation in strong fields and thus allows us to study polyatomics more readily, such as the four-atom formyl chloride cation, $ClCHO^+$ (see Figure 2A for its
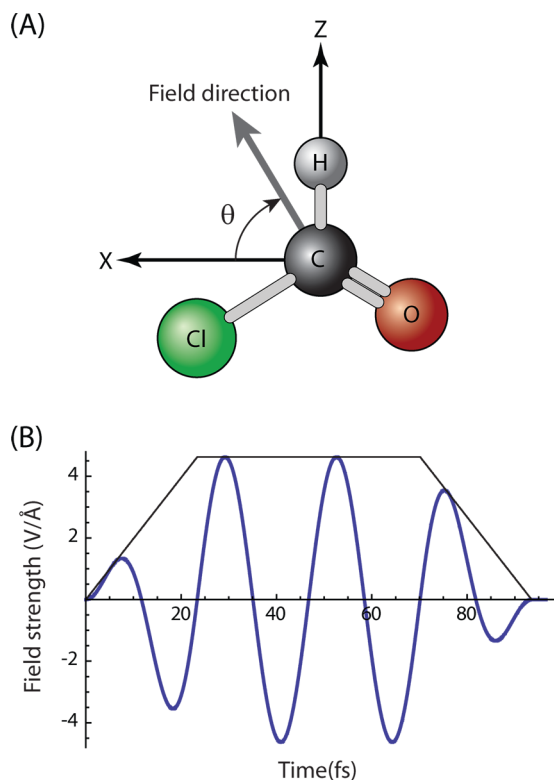
Figure 2. The formyl chloride ion structure and the laser pulse. (A) The molecular structure of $ClCHO^+$, the coordinate system and the definition of θ, the angle between x-axis (perpendicular to C−H bond) and the field direction. (B) The temporal evolution of the laser electric field.

structure). One of the main reasons for choosing cations instead of neutral molecules in this study is to avoid the competition from ionization, which usually dominates strong field processes in neutrals with a laser intensity of 10^{14} W/cm². With a much higher ionization potential in cations, the ionization probability generally falls below 10%, while the dissociation probability is close to 100% (see later discussion). Also, as we will discuss later, the competition from ionization can be further suppressed due to delayed dissociation that takes place after the pulse. Therefore, ionization can reasonably be

neglected. The calculations are restricted to the ground electronic state of the cation. The calculations are performed using the development version of the Gaussian program[21] with the B3LYP/6-311G(d,p) level of theory.

We start by first investigating the statistical decomposition of an energized formyl chloride cation. It can dissociate via three channels: HCl^+ + CO: H + $ClCO^+$: Cl + HCO^+. We first distribute 2.34 eV of energy into the molecule's vibrational degrees of freedom above the zero point energy using microcanonical normal mode sampling. We ran 300 such trajectories without the laser field. The calculated branching ratio among different product channels is 0.21:0.23:0.54 (HCl^+:H:Cl) (Table 1). This correlates well with the threshold

Table 1. The Branching Ratios of Dissociation Channels for $ClCHO^+$ without a Field, with the Field Randomly Oriented, and with the Field in the Molecular Plane[a]

channel	field-free with statistical energy (eV)		random field orientation[d]	fixed field direction (see Figure 2A)	
	2.34^b	1.64^c		$\theta = 0°$[e]	$\theta = 90°$[f]
$H+ClCO^+$	0.23	0.18	0.22	0.12	0.62
$Cl+HCO^+$	0.54	0.71	0.58	0.23	0.32
HCl^++CO	0.21	0.08	0.05	0.56	0.02

[a]The laser intensity and the wavelength are 2.9 × 10^{14} W/cm² (corresponding to a maximum field strength of 0.09 a.u.) and 7 μm, respectively. [b]300 trajectories; ca. 2% did not dissociate. [c]100 trajectories; ca. 3% did not dissociate. [d]300 trajectories; ca. 14% did not dissociate. [e]300 trajectories; ca. 3% did not dissociate. [f]100 trajectories; ca. 4% did not dissociate.

dissociation energies of the three product channels, which are 1.34, 1.26, and 0.3 eV for HCl^+ elimination, H elimination, and Cl elimination, respectively. We also obtained the dissociation time by setting the dissociation criterion to the separation of two fragments of at least 5.3 Å (10 bohr). The results are shown in Figure 3A. Most of the dissociations occur in less than 400 fs, even for the slower Cl and HCl^+ elimination reactions. This shows that the statistical distribution of the initial energy does not necessarily bar fast dissociation. Instead, at lower available energies, the dissociation is speed-limited by the random fluctuation among different vibrational modes in order to accrue enough energy along specific reaction coordinates, consistent with statistical theories of unimolecular decomposition. In this case, product channels with low energy thresholds are strongly favored. Further calculations with lower available energy (1.64 eV above zero point energy) confirm this: the Cl yield becomes ~10 times greater than HCl^+ elimination (see Table 1). It is also interesting to note that while the H elimination is considerably faster, Cl and HCl^+ eliminations have almost the same dissociation time. This can be understood as follows: the formation of the HCl bond requires the chlorine atom to move away from the carbon atom (C−Cl bond breaking) first; the motion of chlorine is slower and thus it is the "rate-determining" motion. From these calculations, we also obtained the correlation between particular product channels and the initial energy in the different vibrational modes (see Supporting Information Figure S1A). In particular, the HCl^+ elimination channel correlates with elevated initial energy in the C−H rocking motion and C−Cl stretching motion. This is not surprising because HCl^+ elimination requires both the breaking of the C−Cl bond and
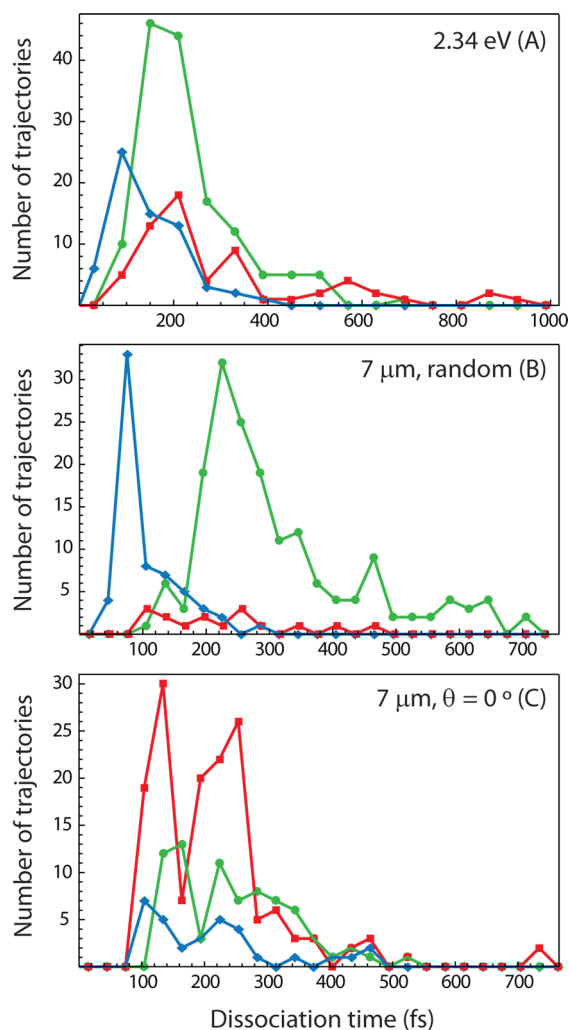
Figure 3. Dissociation times (the fragments are considered dissociated when they are 10 bohr apart) for trajectories (A) with 2.34 eV vibrational energy above zero point, (B) with field randomly oriented, and (C) with the field direction of 0°. The laser field is used with the intensity of 2.9×10^{14} W/cm^2 (corresponding to the maximum field strength of 0.09 au) at 7 μm. Red, blue, and green correspond to HCl$^+$, H, and Cl elimination, respectively.

varying somewhat depending on specific channels (see Supporting Information Table S1 and Figure S2).

Next, we scanned the angle between the laser polarization and the molecule (see Figure 2A for axis definition) from 0° to 360° and obtained branching ratios for each angle (100 trajectories each, except for 0° at which a total of 300 trajectories were computed). The polarization of the laser and the formyl chloride cation are in the same plane. The resulting yields of each product channel are shown in Figure 4A. A large
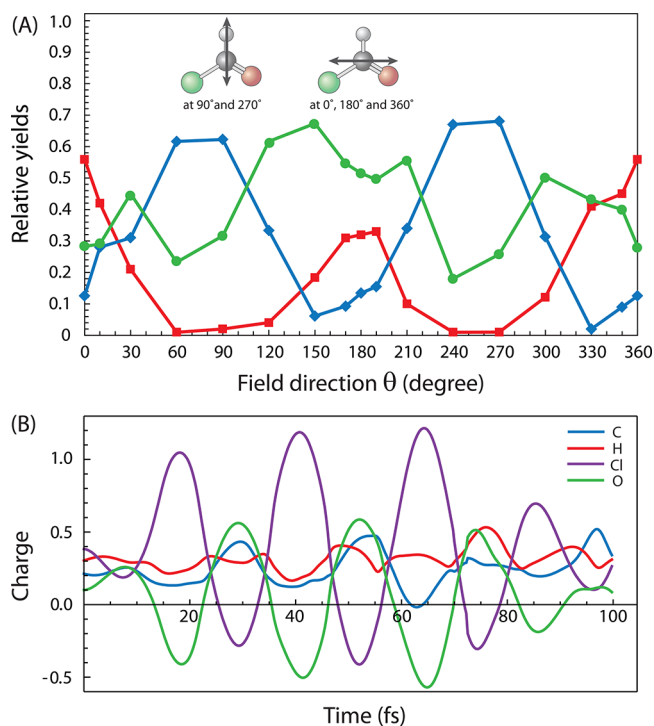
Figure 4. The relative yields and charge evolution in formyl chloride ions. (A) The relative yields for three dissociation channels as a function of the field directions. θ is the angle between the x-axis and the field direction. Red (square), blue (diamond), and green (circle) correspond to HCl$^+$, H, and Cl elimination, respectively. (B) The temporal evolution of the Mulliken charge on Cl (purple), H (red), C (blue) and O (green).

the formation of the H−Cl bond. The transition state can only be reached by the concerted motion between these two vibrational modes. This suggests that we should target these two vibrational modes if the HCl$^+$ elimination channel is desired.

In our laser-driven calculations, we used a trapezoidal shaped pulse containing four laser cycles (Figure 2B), with a peak intensity of 2.9×10^{14} W/cm^2. We obtained the dissociation branching ratios for a three-dimensional randomly aligned ClCHO$^+$ sample using a laser wavelength of 7 μm (single photon energy ~0.18 eV): the Cl dissociation channel dominates the dissociation (70%) while the HCl$^+$ elimination only accounts for 7% of the total dissociation trajectories (Table 1). The branching ratios agree well with those of the field-free calculations with low available energy. The dissociation times are also short (Figure 3B), showing that a large amount of energy has been pumped into the molecules within the pulse duration of ~100 fs. This can be seen from the total energies of the fragments, which amount to a few electron volts,

variation is immediately obvious. When the laser polarization lies along the C−H bond, the H production is dramatically enhanced to ~70%, while the energetically favored Cl elimination is reduced to only ~25%. When the laser polarization is along the C−Cl bond, the Cl elimination has over 70% yield while H production is minimized. What is striking is that the yield of HCl$^+$ almost reaches 60% when the laser polarization is at 0° (i.e., ~30° from the C−Cl bond and 90° from the C−H bond). This represents more than 1 order of magnitude increase of the yield compared to the random alignment case (Table 1). A close inspection of the trajectories leading to HCl$^+$ uncovers two common features: the C−H rocking motion and the stretching of the C−Cl bond (see Supporting Information Figure S1B for the atomic displacements of these two modes). However, the mechanisms leading to the excitation of these two motions are different. Figure 4B shows the charge evolution of the H, C, O, and Cl atoms in the laser field. While the chlorine charge fluctuates significantly between +1.2 to −0.3, the hydrogen charge barely changes (ca. +0.3). The large charge fluctuation in chlorine allows it to

absorb energy from the laser field and thus stretches the C−Cl bond continuously; the hydrogen can only have a quivering motion driven by the laser field. These two vibrational motions are indeed closely coupled to the reaction coordinate of HCl$^+$ elimination: faster rocking motion brings the hydrogen atom close to the chlorine atom, while the C−Cl bond is slowly elongating (see Supporting Information Figure S3 for a few snapshots of a typical trajectory). Interestingly, if the field direction is changed by 180°, equivalent to a 180° change in phase, the HCl$^+$ yield is reduced by half while Cl elimination dominates again. This shows that "timed" motions between these two vibrations are needed to enhance the molecular elimination. While experimentally it is very challenging to implement both laser phase control and molecular orientation, with only molecular alignment, the yield of HCl$^+$ is still enhanced more than 6-fold (Figure 4A). It is also worth noting that the HCl$^+$ yield is strongly dependent on the driving laser wavelength (see Supporting Information Figure S4), and 7 μm is the wavelength at which the yield is the highest. The C−H rocking has a frequency corresponding to a wavelength of 8.5 μm under field-free conditions. Therefore, 7 μm represents a significant blue shift from the resonance wavelength. It is likely that this shift is also due to the requirement of concerted motions between the C−Cl stretching and C−H rocking.

The dissociation times of the three product channels at a polarization angle of 0° are shown in Figure 3C. All reactions take place within 500 fs (corresponding to a reaction rate greater than $\sim 10^{12}$/s). An important result is that most trajectories (>90%) leading to HCl$^+$ production finish after the laser pulse. Even if the dissociation criterion is changed from 10 bohr to 6 bohr, more than 70% of the HCl$^+$ is produced after the laser pulse. Because such delayed dissociations still take place within 500 fs, IVR is not a concern. However, this provides a huge advantage in the process of strong field induced dissociation: it is actually *field-free dissociation*. It has been shown that strong field ionization can be dramatically enhanced when bond lengths are stretched due to charge resonance enhanced ionization (CREI)[22], as has been observed in diatomic and linear triatomic molecules.[23] Even though the general applicability of CREI in polyatomic system is still unclear, such mechanisms will play no role if most of the nuclear rearrangement (bond stretching) happens after the pulse. In fact, a close inspection of the dissociation time reveals that the majority of the trajectories of all product channels finish after the laser pulse. This has interesting implications and suggests that strong field-induced dissociation might be modeled by first putting energy into specific vibrational modes using a field-dependent simulation during the pulse, then running the classical propagation under field-free conditions after the pulse. This approach reduces the major problem in using ab initio methods with atom-centered basis functions to simulate molecular dynamics in strong fields due to their difficulty in treating ionization and nonadiabatic transitions.

While delayed dissociation circumvents the dynamical ionization enhancement effects such as CREI, we can show that the ionization rate is also low in the absence of these effects. To estimate the ionization probability, we sampled several geometries within laser pulses from a trajectory to calculate the average ionization potential (IP > 20 eV) at the CCSD/6-311+G(2df,2pd) level of theory, and calculated the ionization rate using a modified ADK model.[24] The estimated ionization probability of ClCHO$^+$ is about 6% after integrating over the laser pulse. This small ionization probability can be

safely ignored when compared to the almost 100% dissociation probability (also see Supporting Information for a discussion on excitation probability).

A contrasting study was also carried out with a 2 μm driving laser. In order to rule out the pulse duration effect, we used a laser pulse with 14 cycles, which had a similar pulse duration ($\sim$93 fs) as the four-cycle 7 μm laser pulse. One hundred trajectories were run for this shorter wavelength laser pulse with the laser polarization fixed at 0°. Only Cl dissociation was observed in the calculation, showing that the longer driving laser wavelength is indeed more efficient in depositing kinetic energy in molecules to promote mode-selective chemistry.

Now we turn to a discussion of the potential experimental implementation of our proposed method. Two major components are required: a tunable ultrashort mid-IR laser, and techniques that can align (or orient) molecular samples. Both of these techniques are currently within reach. The most direct way to produce an ultrashort mid-IR laser pulse is to use an optical parametrical amplifier (OPA) pumped by a Ti:Sapphire laser. This technique has been widely used to produce milliJoule level ultrashort pulses in the mid-IR range.[25] Other approaches are also being investigated, such as a free electron laser or optical parametrical chirped pulse amplification (OPCPA).[26,27] While there has been no report on the production of ultrashort 7 μm pulses, an extension of current technologies should be able to achieve this. Spatial alignment of molecules can be achieved by both adiabatic and nonadiabatic excitation[28,29] as has been well demonstrated. A high degree of alignment has been achieved using adiabatic excitation.[30] Three dimensional alignment[31] and orientation[32,33] of polyatomic molecules have also been demonstrated. Axial alignment in ions can also be achieved simply by strong field ionization of neutral molecules exploiting the angle dependence of SFI rate.[34,35] Indeed, with the rapid maturing of mid-IR laser technology and molecular alignment techniques, the proposed strong field dissociation method can be implemented in the very near future.

In summary, we propose a new excitation mechanism that can efficiently pump a large amount of kinetic energy into particular modes of molecular systems and accelerate specific chemical reactions that may be energetically or entropically disfavored. The proposed method is general and can be applied in other systems. For example, we have successfully observed promotion of C−F bond fission in CF$_3$Br$^+$ dissociation. This is a classic system in which conventional IRMPD has failed to achieve mode selectivity.[36] We note our method is fundamentally different from the schemes of coherent control implemented with shaped laser pulses and feedback mechanisms,[37−39] in that here, prior knowledge of molecular properties can help devise the appropriate time-dependent laser field, and the subsequent interpretation will be both simpler and offer immediate insight into the molecular reaction dynamics.

■ ASSOCIATED CONTENT

$\mathcal{S}$ Supporting Information

The supporting text describes the calculation results for ruling out electronic excitations during the pulse. One supporting table and four supporting figures are also included. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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