Few-cycle laser pulses to obtain spatial separation of OHF\textsuperscript{−} dissociation products

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In a two-part theoretical study, field-free orientation of OHF\textsuperscript{−} is achieved by means of moderately intense half-cycle, infrared laser pulses. In the first step, a short linearly polarized pulse excites a superposition of rigid rotor rotational eigenstates via interaction with the permanent dipole moment of OHF\textsuperscript{−}. After the field has been switched off, pronounced molecular orientation is observed for several picoseconds. In the second step, femtosecond few-cycle laser pulses are applied to the oriented system to steer vibrational dynamics, modeled by anharmonic vibrational wave functions calculated on a potential energy surface obtained with unrestricted fourth order Møller-Plesset \textit{ab initio} calculations. The result is selective bond breaking of OHF, followed by the spatial separation of dissociation products in the space-fixed frame. Due to revivals in the rotational wavepacket, product yields can be enhanced over long times. © 2009 American Institute of Physics.

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I. INTRODUCTION

Controlling the orientation of molecules in the laboratory frame is desirable for the optimization of bimolecular collision experiments since the position of collision partners determines the outcome of the encounter. Likewise, in unimolecular dissociation experiments, controlling the orientation of molecules is essential for the spatial separation of dissociation products. Surface reactions can likewise greatly benefit from orientation of the gas phase molecules, which allow control of the reaction, site selectivity, insights into the reaction stereospecificity, and in some cases the creation of a molecular orientation involves using a half-cycle pulse (HCP).\textsuperscript{11} In particular, nonadiabatic alignment by means of short (with respect to the rotational periods) laser pulses, introduced in Ref. 8, has been the topic of rapidly growing experimental and theoretical interest during the past decade. Although most of this research focused on isolated linear molecules subject to linearly polarized laser fields, extensions to complex polyatomics, to solutions, to surface adsorbed molecules, and to molecular assembly have been reported, as were extensions to three-dimensional alignment with elliptically polarized fields and to torsional control with circularly polarized light.

Several approaches have been developed to augment the method of nonadiabatic laser alignment so as to affect nonadiabatic orientation. One approach, introduced and examined theoretically in Ref. 9, is based on the combination of a weak static field with a short pulse laser field. Experimental realization of this approach was reported in Ref. 10. Dion \textit{et al.}\textsuperscript{11} applied two-frequency IR laser pulses to orient HCN molecules.

One of the more recent approaches to controlling molecular orientation involves using a half-cycle pulse (HCP). Although this technique has yet only been studied numerically,\textsuperscript{12–15} high-power (0.8 $\mu$) 500 fs HCPs in the terahertz [far-infrared (IR)] range have been available for over ten years and are suitable for nonlinear optics and multiphoton spectroscopy experiments.\textsuperscript{16} In fact, numerical optimal control schemes that produce laser fields based on genetic algorithms have indicated that HCPs are the most effective in achieving a high degree of orientation.\textsuperscript{15}

HCPs rely on a predominantly unipolar electric field that exerts a unidirectional force on the molecular axis. Classically, this force could be considered as a torque applied to a rigid body. An ensemble of randomly oriented molecules will
slowly begin to feel the direction of the electric field, such that the librations of the molecule are restricted to a fixed angular range in $\theta$, the angle between the molecular axis and the field vector. In the long pulse limit where the pulse duration $t_p$ exceeds the rotational period $t_p > \pi \hbar / B_\text{rot}$, where $B_\text{rot}$ is the rotational constant of the molecule in its equilibrium geometry, the dynamics is adiabatic—each eigenstate of the field-free Hamiltonian evolves adiabatically into the corresponding state of the complete Hamiltonian. In the short pulse case $t_p \ll \pi \hbar / B_\text{rot}$, the ensuing time evolution is nonadiabatic and a rotational wavepacket is formed that undergoes dephasing, and rephasing occurs on the time scale of rotational periods.

Our goal in the present theoretical work is to study the application of nonadiabatic laser orientation for bond-selective photochemistry. Specifically, we will apply HCPs to orient OHF$^-$ and subsequently use time-delayed IR and UV pulses to control the branching ratio of the two dissociation channels. Our approach is thus related, on one hand, to the work in Ref. 17 on control of branching ratios through adiabatic alignment, and on the other hand, to the scheme in Ref. 18 that relies on pulses short with respect to vibrational periods to manipulate unimolecular reaction channels.

Several recent articles illustrated the possibility of bond-selective dissociation, using a series of tuned few-cycle IR and UV laser pulses, as shown schematically in Fig. 1 for the case of OHF$^-$. These include the dissociation of isotopically substituted ozone, $^{16}\text{O}^{18}\text{O}^{16}\text{O},^{19}\text{HOD},^{20,21} \text{FHF}^-^{22-24}$, and OHF$^-$. The IR pulse excites a vibrational wavepacket in the ground state. The UV pulse, timed to an instant when the bond to be broken is transiently elongated, electronically excites the wavepacket leading to selective bond breakage (see Fig. 1).

In these studies, the molecule was assumed to be perfectly oriented with respect to the laser fields$^{25,26}$ or randomly oriented$^{19-24}$ In reality neither assumption is realistic, even in a qualitative sense. Perfect orientation is never attained in practice and, moreover, although the nonadiabatic orientation approach provides sharper orientation than other methods, the orientation is transient—the larger the degree of rotational excitation and hence the sharper the orientation the shorter its duration. The assumption of random orientation is also incorrect, as the anisotropy of free space is broken in the presence of the two laser pulses. More importantly, as with similar control schemes, at the absence of orientation one expects (and finds) much less controllability.

Our goal in the present theoretical work is to examine as to what extent laser nonadiabatic orientation can make a useful tool in this and other optical control schemes. We ask also in how far the conclusions in Ref. 25, in which perfect orientation was assumed, survive in the case of practically attainable orientation. We thus recalculate the branching ratio of OHF dissociation products by considering explicitly a rotational-vibrational wavepacket subject to three laser fields, the first of which orients the molecule and the subsequent two selectively break the bond.

The first goal is to achieve a high degree of molecular orientation that is conserved over times much larger than the rotational period $\tau_{\text{rot}}$ of the molecule, which is of the order of 50 ps for OHF$^-$. When molecular orientation is sharp, a series of optimized ultrashort femtosecond bond-breaking pulses is applied to dissociate the oriented molecular bonds. Since rotational motion is negligible on the femtosecond timescale of vibrational dissociation dynamics, molecular fragments will retain their orientation in the space-fixed frame upon dissociation. Furthermore, due to rotational revivals that exhibit a well-defined periodicity under field-free conditions, bond-breaking pulses can be applied whenever a high degree of orientation is obtained, thus leading to a high yield of dissociation products localized in the frame of the laboratory.

On the time scales of relevance, rovibrational coupling has no effect and hence the field-free eigenfunctions are separable into rotational and vibrational components. Our simulation of rotational wavepacket dynamics treats the anion OHF$^-$ as a collinear rigid rotor. The model used in the simulation of vibrational wavepacket dynamics treats both OHF$^-$ and OHF as linear, two-dimensional molecules consisting of the bonds $R_1 = R_{\text{OH}}$ and $R_2 = R_{\text{HF}}$. The dissociation products that can be obtained are O+HF or OH+F. Previously, it was shown that the dissociation of OHF naturally heavily favors the former set of products, while the OH+F products are disfavored due to the topology of the neutral potential energy surface (PES) that has a steep gradient in the O+HF exit channel. Here, we will limit our investigation to optimizing the yields of spatially separated O+HF products.

The remainder of this article addresses the problem of selective bond breaking through control of the rotational and vibrational motions of OHF$^-$. Sections II and III discuss the theory, starting with the rotational dynamics and proceeding to the vibrational dynamics. The methods of quantifying product yields are briefly discussed in Sec. IV, and Sec. V discusses our results. Section VI contains our conclusions.

### II. THEORY: ROTATIONAL WAVEPACKETS

The time-dependent Schrödinger equation for a rigid rotor in the presence of an external laser field is given as...
The field free Hamiltonian is
\[ \hat{H}_0 = B_J \hat{J}^2 \]
and \( \hat{J}^2 \) is the total angular momentum operator squared. The time-dependent interaction \( V(t) \) is given within the electric dipole approximation as
\[ V(t) = -\mu_0 \cos(\theta) \epsilon(t), \]
where \( \mu_0 \) is the permanent electric dipole moment in the space-fixed \( z \)-axis, \( \epsilon(t) \) is the field amplitude, and \( \epsilon(t) \) is an envelope function. The central carrier frequency of the laser pulse \( \tilde{\omega} \) corresponds to an off-resonant IR frequency, such that the molecule remains in the electronic and vibrational ground state. The pulse duration \( t_p \) is defined as
\[ t_p = \frac{\pi}{\tilde{\omega}_p 2 \sqrt{\ln 2}}, \]
such that the central peak includes roughly one-half cycle of the oscillating laser field.

The wave function \( |\Psi(t)\rangle \) is expanded in a complete set of eigenstates of the field-free Hamiltonian \( \hat{H}_0 \),
\[ |\Psi_{J\Omega M}(t)\rangle = \sum_{J\Omega M} C_{J\Omega M}(t) |J\Omega M\rangle e^{-iE_Jt}, \]
where the eigenstates are labeled \( |J\Omega M\rangle \) and \( C_{J\Omega M}(t) \) are time-dependent expansion coefficients depending on the initial state \( |J\Omega M\rangle \). The quantum number of the total angular momentum operator \( \hat{J}^2 \) is denoted as \( J \) and \( \hat{M}_\Omega \) and \( \hat{M}_H \) are the eigenvalues of the projections of \( J \) onto the space-fixed \( z \) and body-fixed \( Z \) axes, respectively. \( E_J \) are the rigid rotor rotational energies,
\[ E_J = B_J (J + 1). \]
The eigenstates \( |J\Omega M\rangle \) of the Hamiltonian can be expressed as normalized rotation fields
\[ |J\Omega M\rangle = \sqrt{\frac{2J+1}{4\pi}} D_{M\Omega}^{J}(\hat{R}), \]
where \( D_{M\Omega}^{J}(\phi, \theta) = (JM|\hat{R}|J\Omega) \) are primitive Wigner matrices and \( \hat{R} = (\phi, \theta, \chi) \) are the Euler angles of rotation describing the position of the body-fixed \( (X, Y, Z) \) frame with respect to the space-fixed \( (x, y, z) \) frame.\(^{27}\)

Substitution of Eq. (7) into Eq. (1) leads to a set of coupled differential equations for the expansion coefficients,
\[ i\hbar \frac{d}{dt} C_{J\Omega M}(t) = \sum_{J'} C^*_{J'\Omega M}(t) \times (J\Omega M| -\mu_0 \cos(\theta) \epsilon(t) |J'\Omega M) \times e^{-iE_{J'}t}, \]
with the initial condition
\[ C_{J\Omega M}(t=0) = \delta_{J J'} \delta_{\Omega \Omega'} \delta_{MM'}. \]
In Eq. (10), both \( M \) and \( \Omega \) are conserved. The use of a linearly polarized laser field implies that \( \hat{M}_H \), the projection of the total angular momentum onto the laser polarization (space-fixed) \( z \) axis, is conserved, \( \Delta M = 0 \). The projection onto the body-fixed \( Z \) axis is conserved \( \Delta \Omega = 0 \) since the electronic state of the molecule does not change. The values \( E_{J'} \) are the rotational energy level spacings,
\[ E_{J'J} = E_{J'} - E_J = B_J [J' (J' + 1) - J (J + 1)]. \]
The interaction Hamiltonian is evaluated according to
\[ \langle J\Omega M| -\mu_0 \cos(\theta) \epsilon(t) |J'\Omega M \rangle = -\mu_0 \epsilon(t) \times W(J\Omega M|J'\Omega M), \]
where \( W(J\Omega M|J'\Omega M) \) is the integral over the Euler angles for the dipole interaction,
\[ W(J\Omega M|J'\Omega M) = \langle J\Omega M| \cos \theta |J'\Omega M \rangle. \]
For moderate field strengths, the electric dipole interaction with the electric field is the leading term and the molecular polarizability—or induced dipole—can be neglected.\(^{28}\)

The total angular momentum \( \hat{J} \) consists of the orbital angular momentum \( \hat{R} \), the electronic angular momentum \( \hat{L} \), and the spin angular momentum \( \hat{S} \), as shown schematically in a vector representation in Fig. 2. The electronic angular momentum \( \hat{L} \) makes a projection \( \Delta \hat{h} \) onto the body-fixed \( Z \) axis, and the spin angular momentum \( \hat{S} \) makes a projection \( \Sigma \hat{h} \) onto the \( Z \) axis, whereas \( \hat{R} \) is normal to the molecular axis. The projection of \( \hat{J} \) onto the body-fixed axis is thus
\[ \Omega = \Lambda + \Sigma \]
In the zero temperature limit, at time \( t=0 \), \( \text{OHP}^- \) is the electronic ground state \(^5\text{II} \) and \( \hat{J} = 0+1 + \frac{1}{2} = \frac{3}{2} \). However, in what follows, we neglect the spin angular momentum, since it makes a very small contribution to the total angular momentum as compared to the orbital component. Therefore, at \( t=0 \) and \( T=0 \) K, we have \( \hat{J} = 1 \). As the laser field is turned on, the field begins to exchange single units of angular momentum with the molecule, i.e., \( \Delta J = \pm 1 \), while the projections \( \hat{M}_H \) and \( \hat{M}_\Omega \) are conserved. Due to the electronic angular momentum \( \hat{L} = 1 \), the total angular momentum of \( \text{OHP}^- \) never drops below \( \hat{J} = 1 \).
Molecular orientation is quantified by examining both the θ dependence of the time-dependent thermally averaged probability density,

\[
|\Psi_{rot}(\theta,t)|^2 = \frac{1}{Q_{rot}} \sum_{J_{\text{min}}=J_{\text{min}}}^{J_{\text{max}}} w_J(T) \int_{0}^{2\pi} |\Psi_{J,\Omega, M}^{rot}(\theta, \phi, t)|^2 d\phi, \tag{16}
\]

where \(\Psi_{J,\Omega, M}^{rot}(\theta, \phi, t) = \langle \hat{R} | \Psi_{J,\Omega, M}^{rot}(t) \rangle\) and the thermally averaged expectation value of \(\cos \theta\),

\[
\langle \cos \theta \rangle_J(t) = \frac{1}{Q_{rot}} \sum_{J_{\text{min}}=J_{\text{min}}}^{J_{\text{max}}} \sum_{M=-J}^{J} \langle \cos \theta \rangle_{J, M}(t), \tag{17}
\]

where \(w_J(t) = \exp(-E_J/k_B T)\) and \(k_B\) is the Boltzmann constant. \(Q_{rot}\) is the rotational partitional function that runs the initial states from \(J_{\text{min}} = 1\) to \(J_{\text{max}}\),

\[
Q_{rot} = \sum_{J_{\text{min}}=J_{\text{min}}}^{J_{\text{max}}} (2J+1) \exp \left[ -\frac{B_J J(J+1)}{k_B T} \right], \tag{18}
\]

where the populations of initial states \(J > J_{\text{max}}\) at the given temperature are negligible (in this work \(J_{\text{max}} = 3\) at \(T = 1\) K). The term \(\langle \cos \theta \rangle_{J, M}(t)\) is evaluated using

\[
\langle \cos \theta \rangle_{J, M}(t) = \langle \Psi_{J,\Omega, M}^{rot}(t) | \cos \theta | \Psi_{J,\Omega, M}^{rot}(t) \rangle = \sum_{J', M'} (C_{J', M'}^{J, M}(t))^* C_{J, M}^{J, M}(t) \times \langle J, \Omega, M | \cos \theta | J', \Omega, M \rangle e^{-iE_{J', \Omega}/\hbar}, \tag{19}
\]

where \(\langle \cos \theta \rangle_{J, M}(t) \in [-1, 1]\). Finally, the term \(\langle J, \Omega, M | \cos \theta | J', \Omega, M \rangle\) can be evaluated using 3-J symbols, \(^{30}\)

\[
\langle J, \Omega, M | \cos \theta | J', \Omega, M \rangle = (-1)^{J+M} \sqrt{(2J+1)(2J'+1)} \times \left( \begin{array}{ccc} J & 1 & J' \\ M & 0 & -M \end{array} \right) \times \left( \begin{array}{ccc} J & 1 & J' \\ \Omega & 0 & -\Omega \end{array} \right). \tag{20}
\]

Large absolute values of \(\langle \cos \theta \rangle\) correspond to a higher degree of orientation in the \(+z\) (or \(-z\)) direction. As the rotational temperature increases, the thermally averaged rotational population

\[
P_{\cos \theta}^J(t) = \frac{1}{Q_{rot}} \sum_{J_{\text{min}}=J_{\text{min}}}^{J_{\text{max}}} w_J(T) \sum_{M=-J}^{J} |C_{J, M}^{J, M}(t)|^2 \tag{21}
\]

contains a broader distribution of \(J\) states and the orientation diminishes.

III. THEORY: VIBRATIONAL WAVEPACKETS

The ensuing control of vibrational dynamics and bond-selective dissociation is modeled using a two-level system consisting of the collinear anion (a) OHF\(^-\) and neutral (n) species OHF. Vibrational wavepackets \(|\Psi_{a}(t)\rangle\) and \(|\Psi_{n}(t)\rangle\), respectively, are obtained as solutions of the time-dependent Schrödinger equation,

\[
\frac{i\hbar}{\partial t} |\Psi_{a,n}(t)\rangle = \left( \hat{H}_{a,n} - \hat{H}_{a,n} \right) |\Psi_{a,n}(t)\rangle. \tag{22}
\]

The molecular two-dimensional Hamiltonian \(\hat{H}_{a}\) or \(\hat{H}_{n}\) for the collinear anionic or neutral molecule, respectively, is given in terms of the bond coordinates \(R_1\) and \(R_2\) by

\[
\hat{H}_{a/n} = -\frac{\hbar^2}{2m_1} \frac{\partial^2}{\partial R_{1}^2} - \frac{\hbar^2}{2m_2} \frac{\partial^2}{\partial R_{2}^2} + \frac{\hbar^2}{m_1} \frac{\partial}{\partial R_{1}} \frac{\partial}{\partial R_{2}} + V_{a/n}(R_1, R_2), \tag{23}
\]

where the first three terms represent the kinetic energy, with the masses \(m_1\) and \(m_2\) given by

\[
m_1 = \frac{m_O \cdot m_H}{m_O + m_H}, \tag{24}
\]

\[
m_2 = \frac{m_O \cdot m_H}{m_O + m_H}. \tag{25}
\]

The term \(V_{a/n}(R_1, R_2)\) is the \textit{ab initio} PES along the coordinates \(R_1\) and \(R_2\).

The field-matter interaction potential \(V(t)\) is given by

\[
\begin{pmatrix} V_a(t) \\ V_{an}(t) \end{pmatrix} = -\mathbf{e}^{\text{vib}} \cdot \begin{pmatrix} \mathbf{\tilde{\mu}}_{an}(R_1, R_2) \\ \mathbf{\tilde{\mu}}_{an}(R_1, R_2) \end{pmatrix}, \tag{26}
\]

where \(\mathbf{e}^{\text{vib}}\) is the vibrational electric field vector.

The permanent dipole moments \(\mathbf{\tilde{\mu}}_{an}(R_1, R_2)\) and \(\mathbf{\tilde{\mu}}_{an}(R_1, R_2)\) are calculated at the same level of \textit{ab initio} theory as the PES \(V_{a/n}(R_1, R_2)\). The coupling terms \(\hat{H}_{an}\) and \(\hat{H}_{na}\) are given by

\[
-\mathbf{e}^{\text{vib}} \cdot \mathbf{\tilde{\mu}}_{an}(R_1, R_2) \quad \text{and} \quad -\mathbf{e}^{\text{vib}} \cdot \mathbf{\tilde{\mu}}_{na}(R_1, R_2)\],

respectively; the values of the anion-to-neutral transition dipole moments \(\mathbf{\tilde{\mu}}_{an}(R_1, R_2) = \mathbf{\tilde{\mu}}_{an}(R_1, R_2)\) can be considered constant for a
given nuclear configuration within the Condon approximation. Here, they are set to 1 for simplicity, but smaller or larger values of the transition dipoles can be compensated by stronger or weaker UV field strengths, respectively. The term \( e_{\text{IR}}(t) + e_{\text{UV}}(t) \) denotes the linearly polarized electric field designed to initiate the vibrational dynamics \( e_{\text{IR}}(t) \), and lead to bond selective dissociation \( e_{\text{UV}}(t) \). The IR field centered about \( t_{0,\text{IR}} \) is given by

\[
e_{\text{IR}}(t) = 2e_{\text{m},\text{IR}} e_{\text{IR}} \cos(\omega_{\text{IR}}(t-t_{0,\text{IR}}) + \eta_{\text{IR}})
\]

for \( t_{0,\text{IR}} \leq t \leq t_{0,\text{IR}} + t_{p,\text{IR}} \) (elsewhere zero). The pulse envelope \( e_{\text{IR}} \) is given by,

\[
e_{\text{IR}}(t-t_{0,\text{IR}}) = \sin^2(\pi(t-t_{0,\text{IR}}) / p_{\text{IR}}),
\]

\( \omega_{\text{IR}} \) is the central pulse frequency, and \( \eta_{\text{IR}} \) is the phase of the IR field. The UV field is identical in form,

\[
e_{\text{UV}}(t) = 2e_{\text{m},\text{UV}} e_{\text{UV}} \cos(\omega_{\text{UV}}(t-t_{0,\text{UV}}) + \eta_{\text{UV}}),
\]

with

\[
e_{\text{UV}}(t-t_{0,\text{UV}}) = \sin^2(\pi(t-t_{0,\text{UV}}) / p_{\text{UV}})
\]

for \( t_{0,\text{UV}} \leq t \leq t_{0,\text{UV}} + t_{p,\text{UV}} \) (elsewhere zero). The time delay between the IR and UV pulses is \( t_{\text{UV}} = t_{0,\text{UV}} - t_{0,\text{IR}} \). In Sec. V, we will retain the notation IR and UV when discussing the parameters of the IR and UV laser fields, respectively. For all pulses, maximum intensities \( I = e_n e_e e_n^e \) are kept under the limit of \( \sim 10^{13} \text{ W/cm}^2 \) to avoid undesired processes, such as double ionization or Stark shifts.

The external electric field thus contains a HCP applied to orient the anion, followed by a sequence of few-cycle IR and UV pulses to initiate the bond-selective dissociation. Prior to excitation by IR and UV fields, the system is in the ground electronic and vibrational state of the anion \( \phi_{\text{an}}^a \).

\[
\begin{align*}
\left| \Psi_a(t > (t_0 + t_{p,\text{rot}})^a) \rightangle &= \left| \phi_{\text{an}}^a \rightangle, \\
\left| \Psi_a(t > (t_0 + t_{p,\text{rot}})^b) \rightangle &= \left| 0 \rightangle.
\end{align*}
\]

IV. THEORY: QUANTIFYING PRODUCT YIELDS

After the laser pulses have been applied and the propagation came to conclusion, the branching ratio of dissociation products \( \text{O}+\text{HF} \) versus \( \text{OH}+\text{F} \) is determined by integrating the probability density of the vibrational wavepacket \( \left| \Psi_n^{\text{ vib}}(t) \right|^2 \) over the triangular grid halves, \( R_{\text{OH}} > R_{\text{HF}} \) and \( R_{\text{HF}} > R_{\text{OH}} \). The probability of dissociation to form \( \text{O}+\text{HF} \), for instance, is calculated as

\[
\text{branch}(t_{\text{end}}) = \frac{\left| \Psi_n^{\text{ vib}}(t_{\text{end}})(R_{\text{OH}} > R_{\text{HF}}) \right|^2}{\left| \Psi_n^{\text{ vib}}(t_{\text{end}})(\text{total}) \right|^2}.
\]

The time-dependent product \( P(\theta, t) \) of oriented dissociation products \( \text{O}+\text{HF} \) is given by

\[
P(\theta, t) = \left| \Psi^{\text{rot}}(\theta, t) \right|^2 \times \text{branch}(t_{\text{end}}),
\]

where \( \left| \Psi^{\text{rot}}(\theta, t) \right|^2 \) is the thermally averaged probability density of the rotational wavepacket at time \( t \), and branch\( (t_{\text{end}}) \) is the branching ratio of the vibrational wavepacket densities obtained after the end of the propagation.

Integrating over \( \theta \) values in the forward and backward hemispheres, one then obtains the space-integrated relative yields for one set of OHF dissociation products

\[
Y_{\text{forward}}(t) = \int_{\theta=0}^{\theta=\pi} P(\theta, t) \sin \theta \, d\theta,
\]

and

\[
Y_{\text{backward}}(t) = \int_{\theta=\pi}^{\theta=2\pi} P(\theta, t) \sin \theta \, d\theta.
\]

The time-dependent relative yield \( Y_{\text{forward}}(t) \) describes the yield of the products O and HF after dissociation in the forward \( 0 \leq \theta \leq \pi/2 \) and backward \( \pi/2 \leq \theta \leq \pi \) hemispheres, respectively, i.e., it is favored for the molecular orientation \( \theta = 0^\circ \) (FH+O). For the reverse orientation \( \theta = 180^\circ \), O+HF, the relative yield \( Y_{\text{backward}}(t) \) is preferred and describes the yield of the products HF and O in the forward \( 0 \leq \theta \leq \pi/2 \) and backward \( \pi/2 \leq \theta \leq \pi \) hemispheres, respectively (see Fig. 1). The same integration could, of course, be carried out to obtain the space-integrated relative yields of the products obtained by breaking the H−F bond, i.e., OH+F and F+HO. Here, we will focus on the products obtained when the O−H bond is broken since this dissociation channel is heavily favored.

V. RESULTS

We first examine the simulation of rotational wavepacket dynamics of OHF− resulting from the application of a HCP with a field strength of \( -500 \text{ MV/m} \) (intensity \( I_{\text{rot}} = 66.4 \times 10^9 \text{ W/cm}^2 \)) to a rotationally cold sample, \( T = 1 \text{ K} \). Our choice of a negative field amplitude is in order for the molecule to orient along the negative z-axis. The rotational constant \( B_r \) for OHF− is \( 0.336 \text{ cm}^{-1} \) leading to a rotational period of \( \tau_{\text{rot}} = \pi h / B_r = 49.6 \text{ ps} \). The \( \text{ab initio} \) permanent dipole moment in the electronic and vibrational ground state of the anion, calculated using unrestricted fourth order Möller-Plesset perturbation theory, is found to be \( \mu_{\text{an}} = 1.05 \text{ D} \), which is directed from F to O, and the corresponding equilibrium bond lengths are \( R_{\text{OH}} = 1.12 \text{ Å} \) and \( R_{\text{HF}} = 1.33 \text{ Å} \).

The pulse frequency is centered at \( \omega_{\text{rot}} = 8.1(2 \pi c) \text{ cm}^{-1} \) (0.243 THz); this IR frequency induces essentially no rotational transitions and is much larger than the spacing between the low-lying rotational energy levels of OHF−. 4\( B_r \), 6\( B_r \), .... The pulse duration \( t_{\text{rot}} \) is chosen to contain approximately one half of the optical cycle and be short compared to the rotational period \( \tau_{\text{rot}} \). Here we use a Gaussian-shaped pulse with duration \( t_{\text{rot}} = 1.2 \text{ ps} \) centered at \( t_0 = 10.0 \text{ ps} \).

The HCP is shown in panel (a) of Fig. 3; the time-dependent thermally averaged populations of the J states \( P_J(t) \) are plotted in panels (b) and (c). At time \( t = 0 \), nearly 79% of the population is in the state \( J = 1 \) and nearly 19% is in the state \( J = 2 \). Again, due to its \( ^2 \Pi \) groundstate symmetry, OHF− has a minimum total angular momentum of 1 and the state \( J = 0 \) is not allowed. As the laser is turned on, the system exchanges units of angular momentum with the external field, causing population in \( J = 1 \) to spike at \( t = 9.46 \text{ ps} \), i.e., shortly before the peak of the HCP, followed by a spike in...
the population in $J=2$ at $t=9.67$ ps. The population continues to migrate into higher-lying states, such that $P^T_{J=3}(t)$ reaches a value of 0.32 at $t=9.77$ ps and $P^T_{J=4}(t)$ reaches 0.28 shortly thereafter, at $t=9.85$ ps. This sequential rotational excitation, familiar in the area of intense laser alignment, gives rise to a broad rotational wavepacket with specific phase relations among the rotational levels. After the field has been removed [for $t>(t_0+\Delta t)$], the wavepacket consists of $P^T_{J=13}(t)\approx 0.16$, $P^T_{J=10}(t)\approx 0.15$, and $P^T_{J=14}(t)\approx 0.12$, followed by $P^T_{J=11}(t)\approx 0.10$ and $P^T_{J=15}(t)\approx 0.06$ with minor contributions from remaining levels included in the simulation, $J_{\min}=1\leq J\leq 12$ and $18\leq J\leq 30$, such that the total normalized population is contained within $J_{\min}=1\leq J\leq 30$. The wavepacket composition remains constant, while the relative phases of the rotational states continue to clock on the time scale of the rotational period of 49.6 ps. This dephasing and rephasing of the rotational states give rise to a rotational revival structure that persists as long as coherence is maintained.

The orientation cosine corresponding to this wavepacket propagation is plotted in Fig. 4(a). At $t=0$, the orientation cosine is 0, indicating an isotropic distribution of the wave function. As the field is turned on, the behavior of $\langle \cos \theta \rangle(t)$ is coherent, but the rapid oscillations reflect the large number of angular momentum states that compose the rotational wavepacket. The rotational period of $\sim 50$ ps is clearly observable.

The thermally averaged normalized rotational wavepacket probability density $|\Psi^{\text{th}}(\theta,t)|^2 \sin(\theta)$, calculated at $T=1$ K, is shown for several times during the dynamical evolution in Fig. 4(b). At $t_1=0$ ps, the wavepacket is isotropic, with probability density distributed symmetrically about $\theta=90^\circ$. As the pulse is turned on, an oriented rotational wavepacket is created. After the laser field has been turned off [$t>(t_0+\Delta t)$], the composition of the wavepacket remains...
constant but the phases of the rotational states continue to clock, leading to dynamical behavior of the wavepacket probability density as a function of the orientation angle \( \theta \). At the orientation extrema, \( t_2 = 11.1 \text{ ps} \) and later instances spaced by the revival time \( \tau_{\text{rev}, \theta} \), \( \langle \cos \theta \rangle(t) = -0.72 \) and the probability density is strongly focused in the backward hemisphere \((\pi/2 \leq \theta \leq \pi)\), corresponding to orientation along the negative space-fixed \( z \)-axis. At \( t_3 = 59.1 \text{ ps} + n \tau_{\text{rev}, \theta}, \ n = 0, 1, \ldots, \langle \cos \theta \rangle(t) = 0.70 \), and the probability density is centered around 20°. When the orientation cosine \( \langle \cos \theta \rangle(t) \) passes through zero, e.g., at \( t_3 = 41.9 \text{ ps} \), \( |\Psi^n(\theta, t)|^2 \sin(\theta) \) contains a mixture of states distributed between both forward and backward hemispheres, such that the orientation observable averages to zero.

Next, a series of optimized ultrashort IR+UV laser pulses is applied to the oriented system. The pulses are designed so as to optimize the dissociation of \( \text{OHF}^- \) into the products \( \text{O}+\text{HF} \). The IR and UV field intensities are optimized to \( I_{\text{IR, vib}} = 2.7 \times 10^{12} \text{ W/cm}^2 \) \( (\epsilon_{\text{IR, vib}} = 3.2 \text{ GV/m}) \) and \( I_{\text{UV, vib}} = 6.6 \times 10^{12} \text{ W/cm}^2 \) \( (\epsilon_{\text{UV, vib}} = 5 \text{ GV/m}) \), respectively. The frequency of the IR pulse, \( \omega_{\text{IR, vib}} = 1565 \text{ (2\pi cm}^{-1}) \), is tuned to drive the asymmetric stretching vibration and contains the mean energy spacing between the asymmetric vibrational eigenfunctions. Other parameters of the IR pulse are \( \eta_{\text{IR, vib}} = 0 \) and \( \tau_{\text{IR, vib}} = 50 \text{ fs} \). After a time delay \( t_3 = 19 \text{ fs} \), the vibrational wavepacket created by the IR pulse has been strongly displaced from the equilibrium position and \( R_{\text{OH}} \) has been extended to 1.18 Å. This time corresponds to almost the end of the first complete cycle of the IR pulse. At this instant an ultrashort UV pulse with \( \tau_{\text{UV, vib}} = 5 \text{ fs} \), \( \eta_{\text{UV, vib}} = 0 \), and a carrier frequency corresponding to the vertical energy spacing between the PESs \( V(\text{OHF}^-) \) and \( V(\text{OHF}) \) \( (\omega_{\text{UV, vib}} = 28228 \text{ (2\pi cm}^{-1}) = 3.5h^{-1} \text{ eV}) \) photodetaches the electron. A neutral wavepacket is prepared along the \( \text{O}+\text{HF} \) dissociation channel of \( \text{OHF}^- \) and nearly exclusive \( \text{O}+\text{HF} \) neutral dissociation results. It is preferable to excite the system a few femtosecond before the IR cycle is completed, so that the maximum displacement of the H atom coincides with the maximum intensity of the IR pulse. At the end of the propagation, the wavepacket remains relatively compact and the final calculated branching ratio at \( t = t_{0, \text{IR}} + 70 \text{ fs} \) is 98.2.

The tuning of the delay time \( t_d \) is critical for optimized wavepacket dissociation. By varying \( t_d \), shorter or longer times, the optimized dissociation behavior will be manipulated. For delay times shorter or longer than \( t_d \), the wavepacket is not compactly located at the turning point of its oscillation. As a result, the frequency of the UV pulse tuned to match the energy spacing \( V_n - V_u \) at the time \( t_d \) is no longer valid and the efficiency of the photodissociation pulse is diminished. Since the vibrational wavepacket requires of the order of 20 fs to complete one oscillation, the delay time should be tuned within \( \pm 2 \text{ fs} \) of \( t_d \) for maximum photodissociation yield.

Above we have considered the effect of varying the angle \( \theta \) between the molecular dipole vector \((+Z \text{ axis})\) and the space-fixed \(+Z \text{ axis}\). An alternative yet equivalent method of manipulating the field-matter interaction is by modulating the phase \( \eta_{\text{IR, vib}} \) of the central carrier field of the IR pulse. In other words, for the field given in Eq. (27), phases \( \eta_{\text{IR, vib}} = 0° \) and \( \eta_{\text{IR, vib}} = 180° \) will cause the wavepacket to oscillate in opposite directions, similar to opposite orientations of the molecular axis in the space-fixed frame. The resulting bond stretching is driven in the first case toward an extension of the \( R_{\text{HF}} \) bond, in the second toward an extension of the \( R_{\text{OH}} \) bond, as shown in Fig. 5.

We proceed to analyze the wavepacket dynamics resulting from pulses simulated with opposite phases \( \eta_{\text{IR, vib}} \). For \( \eta_{\text{IR, vib}} = 0° \), \( R_{\text{OH}} \) has been extended on the anion PES from its equilibrium length of 1.12 to 1.18 Å, while \( R_{\text{HF}} \) has been compressed from its equilibrium length of 1.33 to 1.27 Å, leading to a wavepacket that is compactly located beneath the transition state point of the neutral PES, as seen in Fig. 5. On the other hand, when \( \eta_{\text{IR, vib}} = 180° \), the opposite is true, namely, \( R_{\text{OH}} \) has been compressed to 1.06 Å and \( R_{\text{HF}} \) has been extended to 1.38 Å. The wave functions that are excited at \( t = t_{0, \text{IR}} + 19 \text{ fs} \) to the neutral surface \( V(\text{OHF}) \) for \( \eta_{\text{IR, vib}} = 0° \) and \( \eta_{\text{IR, vib}} = 180° \) behave, accordingly, to their dynamics on the anion PES, see Fig. 6. In the case of excitation to the neutral PES for \( \eta_{\text{IR, vib}} = 180° \), the wave function has a slight tail in the direction of the \( O+HF \) dissociation channel. In the case \( \eta_{\text{IR, vib}} = 0° \), as the compact wavepacket proceeds to evolve on the dissociative surface, the ensuing stretching of \( R_{\text{OH}} \) and compression of \( R_{\text{HF}} \) for \( t + t_{0, \text{IR}} > 19 \text{ fs} \) lead to a more effective dissociation along the \( O+HF \) channel.

Finally, the relative yields \( Y_{\text{forward}}(t) \), \( Y_{\text{backward}}(t) \), and \( Y_{\text{forward}}(t) + Y_{\text{backward}}(t) \) of dissociation products, calculated according to Eqs. (34) and (35), are shown in Fig. 7. The forward and backward \( Y(t) \) yields follow the time evolution of the rotational wavepacket shown in Fig. 4(a), undergoing

![FIG. 5. Calculated expectation values of bond lengths \( R_{\text{HF}} \) and \( R_{\text{OH}} \) on the anion PES for \( \eta_{\text{IR, vib}} = 0° \) (dashed) and \( \eta_{\text{IR, vib}} = 180° \) (solid). The vibrations are out of phase by a factor of \( \pi \), leading to vibrational motion toward the transition state in the case of \( \eta_{\text{IR, vib}} = 0° \) and away from the transition state for \( \eta_{\text{IR, vib}} = 180° \).](image-url)
although it is maximized when the molecule is oriented in the positive $z$-axis, corresponding to the dipole vector pointing along the direction of the dissociating laser field. It follows that the modulation depth in the total yield curve, however, depends on the extent to which the ratio of Eq. (32) varies with the relative elongation of the two bonds whose dynamics are controlled. Thus, the degree to which the control approach alters the field-free $\theta$-integrated yield in a given channel would vary from molecule to molecule and would depend on the details of the neutral state PES. For the example considered here, the steep gradient of the neutral state PES favors the O+HF dissociation channel. Consequently the branching ratio of Eq. (32) is close to 1 regardless of $\theta$, although it is maximized when the molecule is oriented in the negative $z$-direction. It follows that the modulation depth of $Y_{\text{forward}}(t)+Y_{\text{backward}}(t)$ is small. Systems such as HOD, for which dissociation channels are nearly equivalent, lead to a much sharper variation in the total integrated yield.\footnote{1} \footnote{2}

VI. CONCLUSION

We have designed a laser scheme consisting of half-cycle and few-cycle laser pulses to control the molecular orientation and ensuing selective bond breaking of a triatomic system. The theoretical approach is based on nonadiabatic orientation of the dipole moment of the molecule along the electric field vector of a UV pulse tuned to resonance between the initial states with a dissociative PES. An IR pulse, timed to a period where the molecule is oriented, induces vibrational wavepacket dynamics in the course of which the two molecular bonds are elongated and contracted out of phase. The short UV pulse dissociates the molecule at instances where a desired of the two bonds is elongated, leading to selective bond breakage. The approach can be regarded as an example of a class of control and spectroscopic schemes that utilize the ability of current technology to probe or trigger events in the molecular frame by orienting the molecule with respect to the laboratory frame. It relies on the time-scale disparity between the rotational and vibrational periods and on the availability of laser pulses that are much shorter than vibrational periods. Due to the former feature, the orientation duration can always be chosen long with respect to the vibrational period, and hence the orientation is stationary on the time scales of relevance. Due to the latter feature, dissociation can be triggered on a time scale on which the vibrational motion is essentially stationary.

In the future, one could envision a laser-driven “distillation” of spatially separated chemical products, i.e., for the purification of chemical mixtures or the targeted deposition of molecules or atoms onto a surface.

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\footnote{5} R. C. Estler and R. N. Zare, J. Am. Chem. Soc. 100, 1323 (1978).
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