

Ultrafast electron diffractive imaging of the dissociation of pre-excited molecules

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Gas phase ultrafast electron diffraction (GUED) has become a powerful technique to directly observe the structural dynamics of photoexcited molecules. GUED reveals information about the nuclear motions that is complementary to the information on the electronic states provided by spectroscopic measurements. GUED experiments so far have utilized a single laser pulse to excite the molecules and an electron pulse to probe the dynamics. This limits the excited states that can be studied to only those that can be reached by absorption of a photon from the ground state or in some cases simultaneous absorption of multiple photons. A broader class of experiments and dynamics can be accessed using two time-delayed laser pulses to access unexplored regions of the potential energy surfaces. As a proof-of-principle experiment using a double excitation, we studied the photodissociation of trifluoroiodomethane molecules that are pre-excited with an infrared (800 nm) femtosecond laser pulse before photodissociation is triggered with an ultraviolet (266 nm) femtosecond laser pulse. We have observed significant differences in the dissociation dynamics, with pre-excitation resulting in a slower dissociation process. This capability can offer insights into the evolution of nuclear wave packets in regions of the excited potential energy surface that are inaccessible in single-photon excitation. We present a methodology to carry out the measurement, analyze, and interpret the data that could be applied to a broad class of experiments.

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I. INTRODUCTION

Gas phase ultrafast electron diffraction (GUED) has become a powerful tool to determine the nuclear motions and relaxation dynamics of photoexcited molecules [1–6]. GUED is directly sensitive to the nuclear geometry of the molecules and thus complementary to spectroscopic measurements that capture changes in the electronic state. GUED provides high spatial and temporal resolution, and the diffraction observable is straightforward to calculate, making it an ideal tool to capture coherent structural changes and to benchmark theoretical calculations of molecular dynamics. The early GUED work of the Zewail group demonstrated the capability to observe transient states and reaction kinetics with picosecond temporal resolution [7,8]. The next milestone was the direct observation of nuclear motions during a photochemical reaction, which required femtosecond resolution. The use of radio-frequency (RF) accelerators to deliver relativistic electrons with mega-electron-volt (MeV) kinetic energy has enabled GUED to achieve a temporal resolution of 150 fs [9–11], and more recently less than 100 fs [12,13]. Through the use of RF compression cavities [14,15] and optical compensation of the electron-laser velocity mismatch, subrelativistic GUED with

kilo-electron-volt (keV) electrons reached a temporal resolution of 240 fs [16,17]. The femtosecond temporal resolution has enabled major scientific advances such as imaging the splitting of a nuclear wave packet at a conical intersection [3], the simultaneous observation of changes in the nuclear and electronic configurations [18], capturing coherent nuclear motions in photoexcited molecules after they return to the ground state [2,19], and following the structural rearrangements in ring opening reactions in real time [20,21]. Recently, more advanced analysis methods and improvements in data quality have enabled studies on more complex reactions involving larger molecules and multiple reaction channels [22–24]. GUED has also been used to record three-dimensional molecular images and to study rotational wave packets [1,16,17,25]. More recently, the capabilities of GUED have been extended to investigate dynamics triggered by ionization through the use of *ab initio* scattering calculations and more advanced data analysis methods [26,27]. The method has also been extended to studying liquid phase samples [28,29] resulting in ground-breaking studies on the dynamics of liquid water [30]. Thus far, improvements in GUED capabilities have led to compelling scientific advances by revealing key details of the relaxation dynamics or by opening avenues of research. There remains an important limitation to the type of experiment that can be carried out with GUED, i.e., the use of a single pump laser pulse to prepare the excited state to be studied. Introducing a pair of time-delayed pump laser pulses would enable additional capabilities to prepare the sample and probe the dynamics. For example, two pulses could be used to vibrationally pre-excite the molecules and alter the reaction dynamics and products [31–33], to prealign the molecules and capture the dynamics in the molecular frame [34], or to

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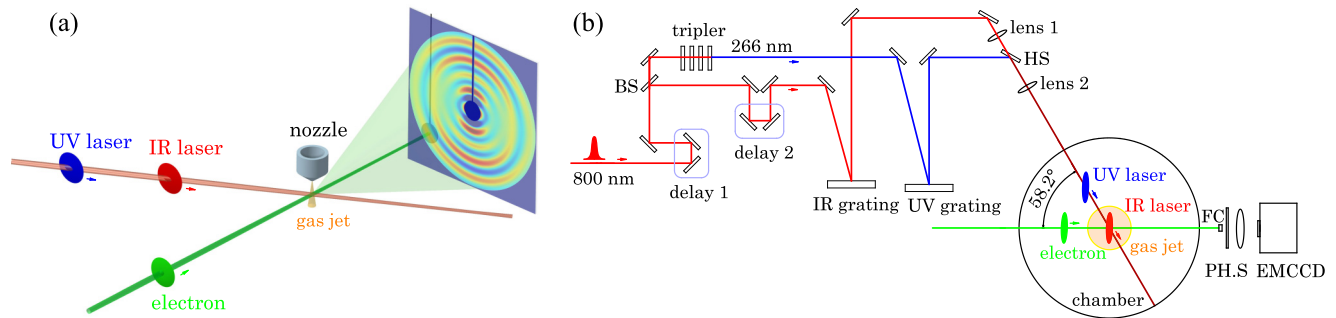


FIG. 1. (a) Diagram of the UED experiment at the interaction region, including the gas jet, the electron pulse (green), the IR laser pulse (red), and the UV laser pulse (blue). (b) Schematic of the experimental layout with IR + UV laser pulses (not to scale). The path drawn in red represents the 800-nm-wavelength beam, while blue corresponds to the 266-nm laser beam, and green corresponds to the electron beam. The electron generation and pulse compression are not shown in this diagram, refer to Appendix A or Ref. [16] for details. A sketch of the electron, IR, and UV beams shows how the velocity mismatch between electron and laser pulses is compensated, in which red, blue, and green represent the IR, UV, and electron pulses, respectively. Arrows indicate the propagation directions. BS: beam splitter; HS: harmonic separator; FC: Faraday cup; PH.S: phosphor screen.

populate an excited state by letting the wave packet evolve after the first excitation and then transferring the population to a different state, or by using a strong field pulse to alter the dynamics [31,35].

Here, we present a proof-of-principle GUED experiment using a pair of time-delayed femtosecond laser pulses to trigger photodissociation dynamics in trifluoroiodomethane (CF_3I) molecules. An IR femtosecond laser pulse is used to pre-excite CF_3I molecules, followed by a UV femtosecond laser pulse that starts a photodissociation reaction, and a femtosecond electron pulse to probe the structural dynamics. We demonstrate the experimental capability and the methodology to retrieve information from changes in both the structure and angular distribution of the molecules. In addition, we demonstrate a time resolution of 150 fs for GUED using a tabletop keV electron source, which significantly improves the previous limit for subrelativistic GUED and matches the temporal resolution of the state-of-the-art relativistic MeV-UED user facility at SLAC National Accelerator Laboratory [9–11].

The UV excitation of CF_3I to the A band, which consists of three repulsive states overlapped in energy denoted as $^3\text{Q}_1$, $^3\text{Q}_0$, and $^1\text{Q}_1$, promotes a nonbonding (n) electron from the iodine atom valence shell to the σ^* antibonding orbital of the C–I bond, resulting in a prompt cleavage of the C–I bond [36–43]. The rapid breaking of the C–I bond of CF_3I molecules happens within 50 fs [3,10].

We use an intense IR femtosecond laser pulse that produces a rovibrational excitation in the electronic ground state of the molecule. Three experiments were carried out to fully characterize the dynamics: using only the UV excitation, using only the IR pulse, and using a double-pulse excitation with IR pulse followed by the UV pulse. We have observed that, when the molecules are pre-excited by the IR laser pulse, the dissociation process is significantly slowed down with respect to the UV-only excitation. We present here the required methodology for carrying out the measurements and analyzing and interpreting the diffraction data that includes multiple excitations and transient anisotropy. This capability significantly advances the state of the art and opens research directions for GUED in which a pair of laser pulses can be

used to prepare excited states that are not accessible with a single laser pulse.

II. METHODS

The experiment was performed using a tabletop keV-UED instrument, which has been described in detail previously [16,44,45]. In the standard configuration, a femtosecond laser pulse (the pump) triggers a photoinduced reaction, and a femtosecond electron pulse (the probe) is used to interrogate the molecules. As shown in Fig. 1, we have modified the setup to accommodate a pair of time-delayed pump pulses. The diffracted electrons, which contain information about the changing molecular structure, are recorded by a two-dimensional (2D) detector. The electron pulse is generated by shining a femtosecond UV laser pulse onto a photocathode. The electron pulse is accelerated to 90 keV in a static electric field and then temporally compressed at the sample position using an RF cavity. Two important modifications in the setup were implemented to carry out this work. First, the temporal resolution was improved to 150 fs through the use of more stable synchronization electronics, and second, the optical setup was modified to accommodate two collinear pump laser pulses with a tilted pulse front at two different wavelengths. The tilted pulse front is necessary to avoid broadening of the temporal resolution as the laser and electron pulses traverse the sample with different speeds. Figure 1(a) shows a diagram of the interaction region including the incident electron and laser pulses, the gas jet, and the scattered electrons that produce the diffraction patterns on the detector.

Figure 1(b) shows a schematic diagram of the optical beam path used to deliver two collinear time-delayed pulses on the sample. An IR laser pulse (800 nm, 7 mJ, 50 fs FWHM) is produced by a Ti:sapphire laser at a repetition rate of 1 kHz. Each laser pulse is split into three separate beams to provide the IR pre-excitation, to generate the UV for photodissociation, and to generate a second UV beam at 266 nm to trigger electron emission from the photocathode in the electron gun (not shown in the figure). The two UV pulses are generated through frequency tripling of the 800-nm beam with beta

barium borate (BBO) crystals. The group velocity mismatch between laser and electron pulses [46,47] is compensated by introducing an angle between the lasers and electron beams and by tilting the pulse intensity front of the IR and UV laser pulses with respect to their phase fronts [16,48]. The tilted front is generated by reflecting the laser pulses from a diffraction grating and imaging the grating surface onto the sample plane, as shown in Fig. 1(b). A more detailed description of the optical setup is presented in Appendix A.

The IR laser pulses on the sample have an energy of 2 mJ per pulse, a pulse duration of ~ 100 fs FWHM, and spot size of 240 μm FWHM, which results in a peak intensity of approximately 1.5×10^{13} W/cm². The UV pulse has an energy of 100 μJ , a pulse duration of 120 fs FWHM, and spot size of 200 μm FWHM. The UV and IR pulses are both polarized in the same direction, which is perpendicular to the plane defined by the propagation directions of the electron and laser beams. We use delay 2 in Fig. 1(b) to adjust the relative time delay between the IR and UV laser pulses. Once this time delay is optimized delay 2 is fixed, and delay 1 is varied to change relative time delay between electron pulse and pair of laser pulses.

The electron beam is guided by a pair of magnetic lenses and deflectors and is truncated by a 300- μm platinum aperture to deliver an electron beam current of 8 pA on the sample, corresponding to 50 000 electrons per pulse. The electron beam diameter is 200 μm FWHM on the sample and the pulse duration is estimated to be 100 fs or less. The instrument response function (IRF) has been characterized to be 140 ± 10 fs (see details in Appendix C). The gas sample, CF₃I, has a purity of 99% and was purchased from Sigma-Aldrich. A de Laval nozzle with inner diameter of 30 μm is used to deliver the sample into the chamber with a backing pressure of 320 torr. The size of the gas jet at the interaction region is estimated to be 250 μm FWHM. The gas jet is orthogonal to the plane defined by the propagation directions of the laser and electron beams. The scattered electrons are captured by a phosphor screen that is imaged onto an electron-multiplying charge-coupled device (EMCCD). The directly transmitted electrons are stopped by a beam stop (Faraday cup) that measures the current of the transmitted electron beam.

III. ELECTRON SCATTERING THEORY

Here, we give a brief overview of the theory of electron scattering and the modified pair distribution function (MPDF) that are relevant for this work (more details can be found in Appendix B). In electron scattering from molecules in the gas phase, electron waves scattered from atoms within the molecule interfere, and the total scattering intensity is an incoherent sum of the diffraction signals from all the molecules in the ensemble. The total scattering intensity I_{total} for a sample of molecules with an anisotropic angular distribution is given by [16,49]

$$I_{\text{total}}(s) = \iint \sum_{j=1}^n \sum_{k=1}^n f_j^*(s) f_k(s) e^{-is \cdot \mathbf{r}_{jk}(\alpha, \beta)} \times g_{jk}(\alpha) \sin \alpha \, d\alpha d\beta, \quad (1)$$

where $f_k(s)$ is the scattering amplitude of the k th atom within the molecule, n is the total number of atoms that constitute the molecule, $\mathbf{r}_{jk}$ is a vector pointing from the k th atom to the j th atom with length equal to the interatomic distance, $g_{jk}(\alpha)$ is the angular distribution of atom pair jk , and s is the momentum transfer vector of the scattered electron. The atomic scattering intensity $I_A(s)$, which is independent of the molecular structure, is given by the sum of the terms with $j = k$, whereas molecular scattering intensity $I_M(s)$ is the sum of terms with $j \neq k$, in which the structural information and angular distribution are encoded. We isolate the time-dependent signal through the diffraction-difference method, given by the difference molecular scattering ΔI_M :

$$\Delta I_M(s, t) = I_{\text{total}}(s, t) - I_{\text{total}}(s, t_0), \quad (2)$$

where the variable t denotes the time delay with respect to the laser excitation and $I_{\text{total}}(s, t_0)$ is the total scattering intensity at time t_0 , which corresponds to a time before the arrival of the laser pulse, i.e., before the sample is excited [17,50]. To separate the changes in molecular structure and angular distribution, we decompose the diffraction pattern into Legendre polynomials [51],

$$\Delta I_M(s, t) = \Delta I_{M,0}(s, t) + P_2(\cos \phi) \Delta I_{M,2}(s, t), \quad (3)$$

where s is the magnitude of the momentum transfer vector s , ϕ is the azimuthal angle on the detector plane, and $P_2(\cos \phi)$ is the second-order Legendre polynomial. $\Delta I_{M,0}(s, t)$ and $\Delta I_{M,2}(s, t)$ are the isotropic and anisotropic components of the molecular scattering, respectively, with their analytic forms given in a prior publication [51]. Here, $\Delta I_{M,0}(s, t)$ captures only the structural changes, while $\Delta I_{M,2}(s, t)$ captures changes in both structure and angular distribution. The contribution from higher-order Legendre polynomials is zero for one-photon excitation, and is negligible for the degree of alignment generated by the IR pulse in our experiment. For the double-pulse excitation, higher orders in the Legendre projection are in principle present but were not used in the reconstruction because their amplitude was found to be very small compared to the lower orders. The Legendre polynomial decomposition can also be used to filter out noise and artifacts in the diffraction signal [17,52]. The normalized difference signal is defined as $\mathcal{R}_m(s, t) = \Delta I_{M,m}(s, t)/I_0(s)$, where $m = 0, 2$ indicates zeroth- or second-order terms, respectively, and $I_0(s)$ is the azimuthally averaged $I_{\text{total}}(s, t_0)$.

The MPDF, which contains both structural and angular information in real space, is produced by the inverse Fourier transform, followed by the Abel inversion, of the rescaled molecular scattering intensity, formulated as $\mathcal{M}(s, t) = s^\kappa I_M(s, t)/I_A$ [3,16,49]:

$$\text{MPDF}(r, \alpha, t) = \text{Abel}^{-1} \text{FT}_{2\text{D}}^{-1} \left[\frac{s^\kappa I_M(s, t)}{I_A} \right], \quad (4)$$

where the value of κ is adjusted to minimize artifacts in the transform and $\kappa = 0.01$ is used below. The MPDF can be understood as an angularly dependent pair distribution function. The atom-pair distance and angular distribution of all atom pairs in real space can be retrieved from the MPDF (see Appendix B for details on the calculations of the MPDF). Furthermore, changes in the structure and angular distribution upon photoexcitation can be retrieved using the difference

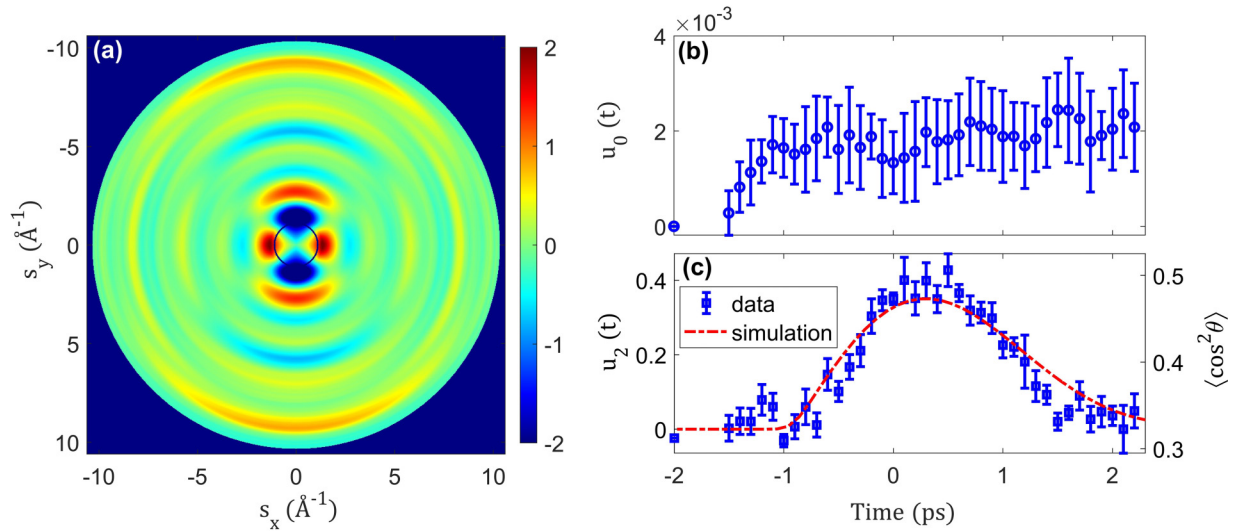


FIG. 2. (a) Experimental pattern $\Delta\mathcal{M}(s)$ of aligned CF_3I molecules at peak alignment, reconstructed from $\Delta I_{M,0}(s)$ and $\Delta I_{M,2}(s)$. The data at small s inside the black circle are not available experimentally and were filled in by extrapolation to 0 at $s = 0$. (b) Time-dependent signal $u_0(t)$. (c) Time-dependent signal of nonadiabatic molecular alignment, $u_2(t)$. The experimental data are represented by blue squares, and the simulation by the red dashed line. The right axis shows the corresponding values of $\langle \cos^2\theta \rangle$. The uncertainties in all figures are the standard deviation of the measurements and are obtained by the bootstrapping method.

MPDF, $\Delta\text{MPDF}(r, \alpha, t) = \text{Abel}^{-1}\text{FT}_{2\text{D}}^{-1}[\Delta\mathcal{M}(s, t)]$, where $\Delta\mathcal{M}(s, t) = s^\kappa \Delta I_M(s, t)/I_A$.

IV. RESULTS

We have carried out three sets of experiments to characterize the molecular response: IR excitation only, UV excitation only, and the combination of IR + UV excitation. We first describe the response of the molecule to the IR pre-excitation, then compare the dissociation dynamics after UV excitation with and without the IR pre-excitation.

A. IR pre-excitation

We use a nonresonant femtosecond IR laser pulse, which creates a rovibrational excitation in the electronic ground state of the molecule. We see evidence of both vibrations and alignment in the diffraction signal after excitation, and we do not observe evidence of dissociation or ionization. The laser pulse produces impulsive alignment of the CF_3I molecules through an induced dipole interaction [53–56]. The maximum degree of alignment is reached approximately 1 ps after the laser excitation, followed by a rotational dephasing on a similar timescale and periodic revivals at later times. The diffraction signal becomes anisotropic when the molecules are aligned, as shown in Fig. 2(a). The IR pulse can also produce a vibrational excitation through nonresonant impulsive stimulated Raman excitation (ISRS) [57–59]. The periods of the vibrational modes of CF_3I are shorter than the instrument response function of the UED instrument. Therefore, the motion cannot be directly time resolved. However, the time-averaged diffraction signal of the vibrating molecule is different from the signal produced by a static molecule because it contains contributions from multiple structures.

A series of diffraction patterns $I_{\text{total}}(s, t)$ with varying time delays between the IR laser and electron pulse, without the

presence of the UV laser pulse, were recorded to capture the time evolution of the diffraction signal. The changes to the molecular structure and the angular distribution can be observed separately using a Legendre decomposition of $\Delta I_M(s, t)$. We extracted the $\Delta I_{M,0}(s, t)$ and $\Delta I_{M,2}(s, t)$ from the measured diffraction patterns, as described by Eq. (3) (details in Appendix D). Figure 2(a) shows the experimental $\Delta\mathcal{M}(s)$ of aligned CF_3I molecules at the time delay of maximum alignment. Here, $\Delta I_M(s)$ was reconstructed from $\Delta I_{M,0}(s)$ and $\Delta I_{M,2}(s)$ using Eq. (3). The main signature of alignment in the scattering pattern is the appearance of anisotropy, which contrasts against the concentric rings seen in the diffraction pattern of randomly oriented molecules. We use the amplitude of the isotropic and anisotropic parts of the signal to map the temporal evolution of the structural changes and the alignment, respectively.

Figure 2(b) shows the amplitude of the sum of the normalized difference signal $\mathcal{R}_0(s, t)$, integrated over a range of momentum transfer where the signal-to-noise ratio (SNR) is highest, from $s_{\min} = 2.3 \text{ \AA}^{-1}$ to $s_{\max} = 3.2 \text{ \AA}^{-1}$, denoted as $u_0(t) = \int_{s_{\min}}^{s_{\max}} \mathcal{R}_0(s, t) ds$. The signal amplitude rises over approximately 300 fs and saturates at a value corresponding to a 0.2% change in the diffraction intensity. The small amplitude of the signal indicates that small structural changes are present, which could be due to small amplitude vibrations and/or minor changes in the equilibrium distances. The signal clearly indicates that there are changes taking place. The zero of time here is set as the time where the alignment signal [Fig. 2(c)] starts to plateau. This setting is the most convenient for the later experiments that include both IR and UV laser pulses (see Sec. IV B).

Figure 2(c) shows the time evolution of the anisotropy, which closely tracks the degree of alignment defined as $\langle \cos^2\theta \rangle$, where θ is the angle between the laser polarization and the molecular axis. The integrated value of $\mathcal{R}_2(s, t)$, $u_2(t) = \int_{s_{\min}}^{s_{\max}} \mathcal{R}_2(s, t) ds$ over the range $s_{\min} = 2.3 \text{ \AA}^{-1}$ to

$s_{\max} = 3.2 \text{ \AA}^{-1}$, was used to map the evolution of the alignment. We interpret the experimental signal by comparison with a theoretical calculation. We have calculated the evolution of the angular distribution of the molecules after the laser excitation by solving the Schrödinger equation (details in Appendix E). The angular distribution was then used to calculate the 2D diffraction signal, from which the $\mathcal{R}_2(s, t)$ was extracted using the same procedure as with the experimental data. The dashed red line in Fig. 2(c) shows the results of the simulated $u_2(t)$, which is in very good agreement with the experimental data. Note that the left axis shows the time-dependent signal $u_2(t)$, and the right axis shows the corresponding values of the degree of alignment $\langle \cos^2 \theta \rangle$. Figure 2(c) shows that the alignment takes approximately 1 ps to reach the maximum value, remains near the maximum for a few hundred femtoseconds, and then decays. The isotropic signal $u_0(t)$ starts approximately 300 fs before the rise of the alignment, and it increases for about 300 fs before plateauing. This indicates that the structural changes are faster than the changes in the angular distribution, which agrees with vibrational motions being faster than rotation.

B. Timing of UV excitation with respect to the IR pre-excitation

The first step before carrying out the two-pulse experiments is to set the relative time delay between the UV and IR pulses. Recording the diffraction signal while the molecules are aligned has the advantage that the angular distribution can be used to distinguish between internuclear distances that are parallel and perpendicular to the alignment axis, which reveals more structural information [3]. Additionally, the excitation yield can be increased if the molecules are aligned such that the transition dipole moment is parallel to the polarization of the excitation pulse. For CF_3I , the transition dipole for excitation to the A band points along the direction of the molecular axis (the C–I axis), which is the same as the alignment axis. One disadvantage of using alignment is that it is more challenging to retrieve information when the alignment is changing during the observation window. Thus, we select the time of arrival of the UV pulse ($t = 0$) to be the time where the alignment first reaches its maximum value. This provides us with a time window of approximately 500 fs after laser excitation to follow the reaction with a constant degree of alignment, which is sufficient to capture the dissociation dynamics. Note that the IR pulse arrives more than 1 ps before the UV pulse so there is no temporal overlap between the pulses, and the dissociation takes place in a field-free environment.

The time delay between the IR and UV pulses was set by separately recording the dynamics after each pulse. As discussed earlier, the UV excitation leads to rapid photodissociation, which produces a clear signal in the diffraction pattern. We define the time zero for the UV-only signal as the time delay when the first changes in the $\Delta I(t)/I_0$ signal become visible. The evolution of the signal $\Delta I(t)/I_0$ is described in detail in Appendix C. We set the relative time delay between the IR and UV pulses such that the time zero of $\Delta I(t)/I_0$ induced by the UV pulse is synchronized to the beginning of the plateau in $u_2(t)$. Figure 3 shows the relative timing of the two signals, where the left axis corresponds to

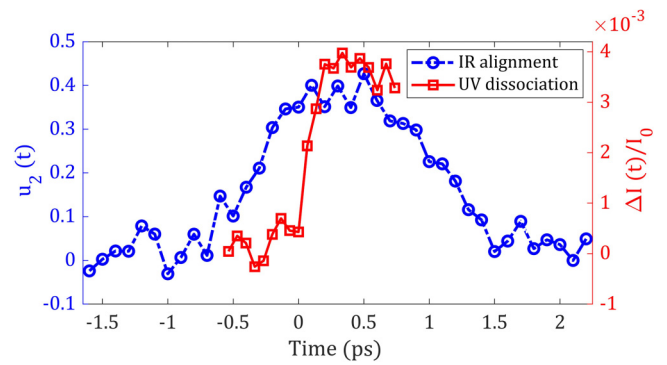


FIG. 3. Synchronizing the maximum alignment in $u_2(t)$ (blue line) to the initial photodissociation characterized by the $\Delta I(t)/I_0$ (red line). Note that the left axis is for $u_2(t)$ and right axis for $\Delta I(t)/I_0$.

$u_2(t)$ and the right axis to $\Delta I(t)/I_0$. In the IR + UV experiment, the time delay between the two laser pulses is fixed while the time delay between the electron pulse and both laser pulses is varied using delay stage 1 in Fig. 1(b).

C. Photodissociation dynamics with IR pre-excitation

Here, we compare the dissociation dynamics for the case of UV-only excitation with the case of dissociation for pre-excited molecules (IR + UV). In both cases, anisotropy is imprinted in the diffraction patterns because molecules along the laser polarization are preferentially excited. The transition dipole for UV excitation lies along the C–I bond direction, resulting in an angular distribution of the excited molecules that follows a $\cos^2 \theta$ dependence, where θ is the angle between laser polarization and the C–I bond. Based on the amplitude of the diffraction signal, we estimate that 1.2% of the molecules are excited by the UV pulse. In the case of IR + UV excitation, the excited molecules are in a narrower angular distribution because there is a contribution from the prealignment of the IR pulse in addition to the angular selectivity of the UV excitation. We first look at the timescale of the photodissociation by extracting the $\mathcal{R}_0(s, t)$ using Eq. (3). This signal captures the structural changes exclusively without the influence of the angular distribution. For the IR + UV measurement, the $I_{\text{total}}(s, t_0)$ in Eq. (2) used for the difference is recorded before the UV pulse but after the IR pulse, at a time ($t = -0.1$ ps) when the molecules are already aligned. The $I_0(s)$ for the denominator is the same for both cases, recorded before both laser pulses. This is done to subtract the contribution to the signal from the alignment induced by the IR laser pulse for better comparison of the two cases.

Figures 4(a) and 4(b) show the time evolution of the normalized difference signal, $\mathcal{R}_0(s, t)$, for the UV-only and IR + UV excitation, respectively. The positive and negative features in the difference signals appear at the same locations in both cases. The signals have higher SNR at lower s because the scattering intensity decreases rapidly as s increases. The changes in the diffraction signal are the result of two structural changes: the separation of the two fragments after breaking of the C–I bond and changes in the structure of the CF_3 fragment. The breaking of the C–I bond produces a significantly stronger

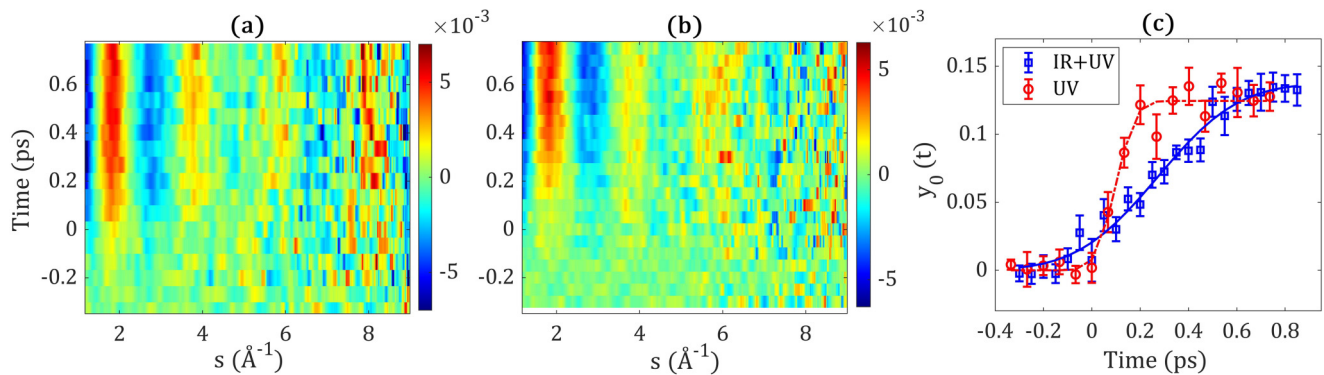


FIG. 4. Normalized difference signal for UV-only and IR + UV excitation. (a) $\mathcal{R}_0(s, t)$ for CF_3I photodissociation initiated in the UV-only experiment. (b) $\mathcal{R}_0(s, t)$ for IR + UV excitation. (c) Comparison of $y_0(t)$ for UV-only and IR + UV excitation. The red circles are data of the UV-only experiment, and the error function model with fitted parameters is the red dash line. The blue squares are the data of the IR + UV experiment, and the blue solid line is the error function with fitted parameters. The uncertainties are the standard deviation obtained by the bootstrapping method.

signal than the changes in the structure of the fragment due to the comparatively high scattering cross section of the iodine atom.

Figures 4(a) and 4(b) show similar signals in both cases because both excitations result in dissociation. There is, however, a clear difference in the timescale, with the UV-only signal having a significantly faster rise time. Figure 4(c) shows a lineout of the rise time of the diffraction signal, denoted as $y_0(t)$, which is calculated by integrating the $\mathcal{R}_0(s, t)$ over the two strongest peaks in the signal, specifically the regions between $1.3\text{--}2.0 \text{ \AA}^{-1}$ and $3.1\text{--}4.3 \text{ \AA}^{-1}$. Fitting an error function (Appendix C) to the $y_0(t)$ lineouts gives a rise time of $150 \pm 41 \text{ fs}$ for the UV-only excitation, while for the IR + UV experiment the rise time is $618 \pm 63 \text{ fs}$. The timescale of the UV-only data is comparable to the IRF of the UED setup, which suggests the dynamics are faster than 150 fs. In the second case, however, the dissociation is slowed down significantly by the pre-excitation. Based on the fits, we estimate an excitation percentage of 1.2% for the UV-only cases and 1.3% for the IR + UV cases. This is consistent with the expectation of a higher excitation yield with prealigned molecules. The slower reaction could be caused by a slower dissociation speed of the fragments, a slower rate of dissociation, or a combination of both. We now investigate the signal in real space to extract more details about the process.

We use Eq. (4) to generate the $\Delta\text{MPDF}(r_x, r_y, t)$ for the UV-only and IR + UV measurements (more details on how the ΔMPDF was calculated can be found in Appendix F), where r_x and r_y are the components of the interatomic distances perpendicular and parallel to the alignment axis, respectively. The geometrical structure of CF_3I in the ground state is shown in Fig. 5(a). The experimental $\Delta\text{MPDF}(r_x, r_y)$ at $t = 0.25 \text{ ps}$ with IR + UV excitation is shown in Fig. 5(b), with blue indicating loss and red indicating gain of atom-pair distances compared to the unexcited molecules. The polarization direction of both IR and UV is along the r_y axis in the figure. The negative rings correspond to the loss of the ground-state atom-pair distances: $r_{\text{CF}} = 1.33 \text{ \AA}$, $r_{\text{CI}} = 2.14 \text{ \AA}$, $r_{\text{FF}} = 2.15 \text{ \AA}$, and $r_{\text{FI}} = 2.89 \text{ \AA}$, whereas the positive rings are due to the atom-pair distances formed during the reaction. The atom-pair angular distribution is represented

by the intensity distribution of the ring. The UV excitation of CF_3I to the A band is stronger for molecules with the C–I axis aligned along the polarization direction of the UV laser (more details in Appendix G). As a result, the signals from the C–I and F–I atom-pair distances, including both loss and gain, appear predominantly along the r_y axis (corresponding to the azimuthal angle $\alpha = 0$). The signal of the C–F and F–F atom pairs appears along the r_x axis, corresponding to the azimuthal angle $\alpha = \pi/2$, perpendicular to the laser polarization. This angular separation is important because it separates the signals from the F–F and C–I distances, which overlap completely in the one-dimensional (1D) PDF.

The dissociation dynamics appear mostly along the direction parallel to the laser polarization; therefore, we integrated the $\Delta\text{MPDF}(r, \alpha, t)$ over the azimuthal angle α from 0° to 10° to capture the changes in the C–I and F–I distances using $\Delta\text{PDF}_{\parallel}(r, t) = \int_{0^\circ}^{10^\circ} \Delta\text{MPDF}(r, \alpha, t) d\alpha$.

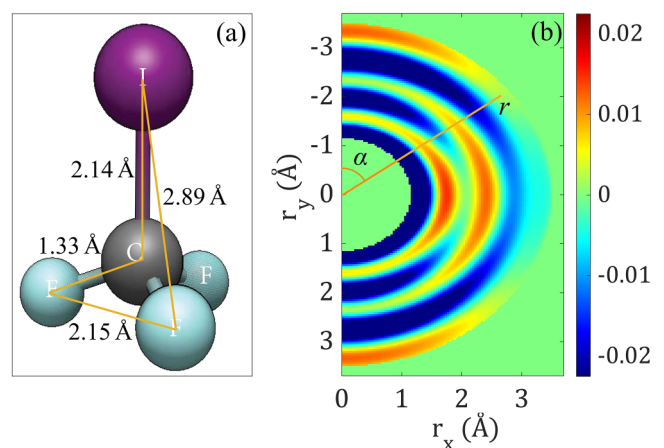


FIG. 5. (a) Diagram showing the structure of CF_3I in the ground state, with atomic labeling by the atom types and atom-pair distances $r_{\text{CF}} = 1.33 \text{ \AA}$, $r_{\text{CI}} = 2.14 \text{ \AA}$, $r_{\text{FF}} = 2.15 \text{ \AA}$, and $r_{\text{FI}} = 2.89 \text{ \AA}$. (b) Experimental $\Delta\text{MPDF}(r_x, r_y, t = 0.25 \text{ ps})$ with IR + UV excitation. Blue indicates loss and red indicates gain of atom-pair distances compared to the unexcited molecules. Polarizations of IR and UV are along the r_y axis, $r = \sqrt{r_x^2 + r_y^2}$ and $\alpha = \tan^{-1}(r_x/r_y)$.

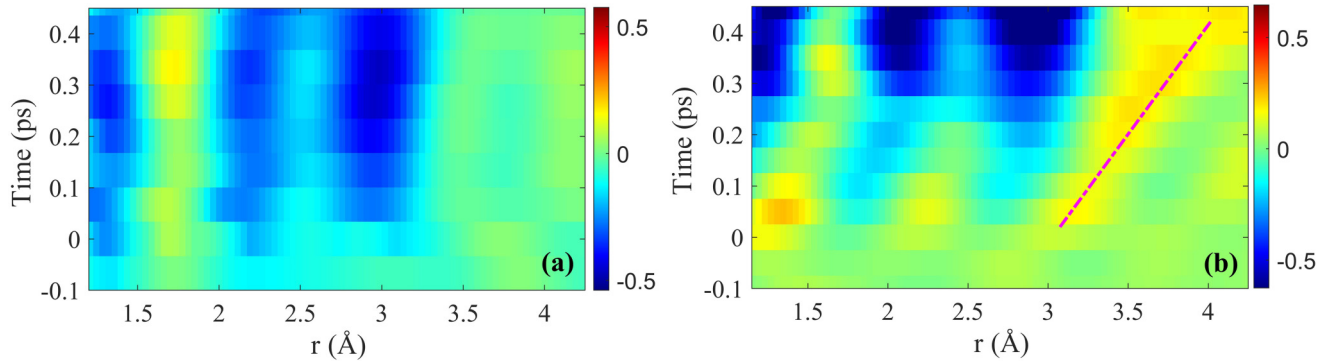


FIG. 6. (a) Experimental $\Delta\text{PDF}_{||}(r, t)$ for UV-only excitation, with blue indicating loss and red indicating gain of atom-pair distances compared to the unexcited molecules. (b) Experimental $\Delta\text{PDF}_{||}(r, t)$ for IR + UV excitation. The positive tilted distribution is the F–I wave packet during the dissociation. The linear function with fitted parameters is the red dashed line.

Figures 6(a) and 6(b) show the $\Delta\text{PDF}_{||}(r, t)$ for the UV-only and IR + UV cases, respectively, over the time range from -0.1 to 0.4 ps. For the later times, both measurements show the depletion signals around $r_{\text{CI}} = 2.14$ Å and $r_{\text{FI}} = 2.89$ Å indicating the loss of C–I and F–I distances due to the dissociation. However, the two signals are very different for the early times. The tilted bands that appear in Fig. 6(b) are due to the gradual increase of the distance between the iodine and CF_3 fragment. The clearest evidence is the bright band, which starts around 3 Å at $t = 0$ and moves toward larger distances at later times. This corresponds to the dissociating wave packet projected into the increasing F–I distance. The same tilted features are not observed in the case of the UV-only excitation [Fig. 6(a)] because the wave packet moves faster and the signal is blurred by the IRF. The dissociation with UV-only excitation is known to take place on a timescale of 50 fs [3,10]. The fast dynamics are reflected in the appearance of the depletion features, and as shown in Fig. 4(c). The depletion signals reach a plateau after 0.2 ps for UV-only excitation. The slower dissociation in IR + UV experiments is also evident in the slow increase in the amplitude of the depletion signals, which is consistent with the analysis shown previously in Fig. 4(c). The real-space analysis, however, allows us to capture the motion of the dissociating wave packet. This suggests that the dissociation process is still predominantly taking place coherently, with a slower dissociation speed of the fragments. The real-space analysis also shows that the direction of the transition dipole moment remains unchanged by the IR pre-excitation since the excited molecules show the same angular distribution peaked along the polarization of the UV pulse.

We extract a dissociation speed of 2.82 ± 0.57 Å/ps based on the movement of the peak corresponding to the F–I wave packet, by a linear fit to the center position of the peak versus time. The red dashed line in Fig. 6(b) shows the linear fit to the data. This speed is markedly slower than the dissociation speed for the UV-only excitation.

In order to validate our interpretation of the real-space signal, we use a simple model in which the iodine atom moves away along the direction of the C–I bond after UV excitation while the structure of the CF_3 fragment remains unchanged. While in reality, we expect the CF_3 fragment to be vibrationally excited, our model focuses on capturing the

effect of the dissociation on the diffraction signal. We first calculated $I_{\text{total}}(\mathbf{s}, \Delta\text{CI})$, where ΔCI represents the increase of the C–I atom-pair distance [60]. Applying the procedures used on the experimental data, we calculated $\Delta I_M(\mathbf{s}, \Delta\text{CI})$ and $\Delta\text{MPDF}(r_x, r_y, \Delta\text{CI})$ to obtain the $\Delta\text{PDF}_{||}(r, \Delta\text{CI})$, as a function of ΔCI (more details in Appendix H). For modeling the UV-only case, the relative speed between the fragments (dissociation speed) was set to 22.5 Å/ps, corresponding to 1.17 eV kinetic energy release, based on previously published *ab initio* calculations [61]. This dissociation speed is consistent with the previously reported translational energy of 1.15 eV for photofragments produced by UV-induced photodissociation of CF_3I [62,63]. Using this dissociation speed, we converted the ΔCI to time to obtain the modeled $\Delta\text{PDF}_{||}(r, t)$. The final step is to apply a convolution in time to match the IRF of the measurement. For this, we use a convolution with a Gaussian function with an FWHM of 150 fs. The same procedure was applied to model the IR + UV data, but in this case, we used the speed of 2.82 Å/ps that was retrieved from the experimental data.

Figures 7(a) and 7(b) show the predicted $\Delta\text{PDF}_{||}(r, t)$ for the UV-only and IR + UV cases, respectively, using the simple model. For the UV-only case, the dissociation signal can be seen clearly before the convolution (not shown here, see Appendix H for the figure) but is completely blurred out when the IRF is considered [Fig. 7(a)]. The calculated signal agrees very well with the experimental signal in Fig. 6(a), with the exception of the appearance of additional signals at shorter distance ($r < 1.5$ Å) in the experiments. These differences are caused by changes in the structure of the CF_3 fragment and also by artifacts that appear at short distances due to the finite s range of the data (more information in Appendix H).

Figure 7(b) shows the calculated signal corresponding to the slower dissociation speed of the IR + UV experiment. The main features in the experimental signal are reproduced by the model, with the tilted bands appearing at early times, and the strong band from the increasing F–I distance moving toward larger distances. This model validates our interpretation of a slow dissociation speed. While the model captures the dissociating wave packet accurately, it does not capture all the details of the dynamics over the first 200 fs. These differences are likely due to vibrations and changes in the CF_3 structure, and possibly due to an initially nonuniform speed of the wave

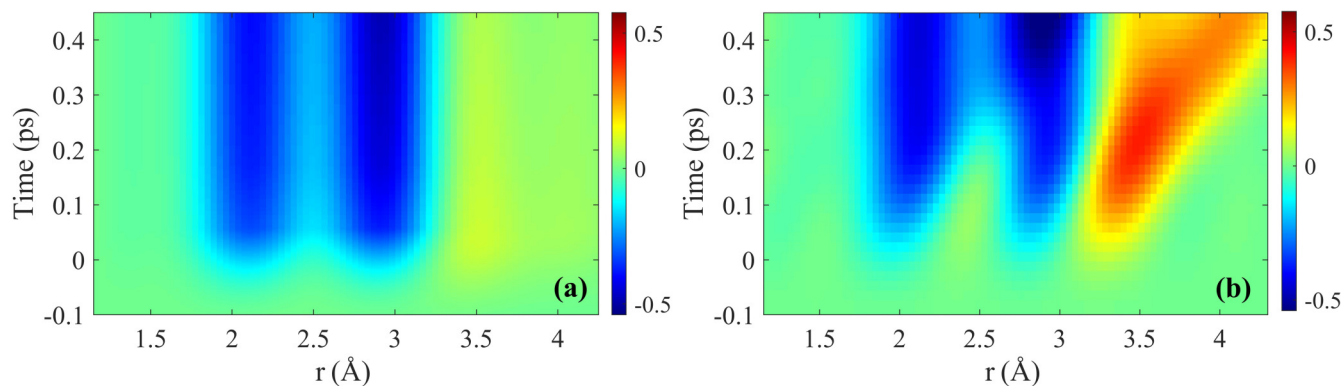


FIG. 7. (a) Modeled $\Delta\text{PDF}_{||}(r, t)$ convolved with a 0.15-ps FWHM instrument response function for the UV-only experiment. (b) Modeled $\Delta\text{PDF}_{||}(r, t)$ convolved with a 0.15-ps FWHM instrument response function for the IR + UV excitation.

packet. We have also tested a different model in which the dissociation speed is the same as in the UV-only case, but we assume a slower statistical dissociation taking place over several hundred femtoseconds, and this model qualitatively disagreed with the experimental data. Thus, we conclude that the dominant process is a coherent dissociation with slower moving fragments. The dissociation wave packet observed corresponds to the F–I distance, which reaches a maximum value of approximately 4 Å during the measurement time window. This corresponds to an increase in the C–I bond distance of approximately 1 Å. Thus, it is possible that the wave packet at this time is still moving in a shallow potential and that the final speed of the fragments will be larger. What is clear from this measurement is that the wave packet is traversing a different region of the potential energy surface (PES).

The IR pre-excitation results in a dissociation channel with slower speed; however, the data indicate that a fast dissociation channel might also be present. While we cannot directly see the wave packet in the fast dissociation channel, we can still distinguish the two channels based on how fast the depletion features appear. This is clear in Figs. 7(a) and 7(b), where we assume only fast and slow dissociation, respectively. The depletion features in Fig. 6(a) quickly reach their maximum value, while in Fig. 6(b) they continue to rise over several hundred femtoseconds. The experimental data for the UV-only excitation [Fig. 6(a)] agree well with the calculation of the fast dissociation only in Fig. 7(a). The depletion signal in the data for the IR + UV excitation shown in Fig. 6(b) is best matched by a combination of the fast and the slow channels. We estimate the contribution of the two channels by calculating the ratio of the amplitudes of the signal corresponding to the F–I dissociation wave packet to the F–I depletion signal. The first originates only from the slow channels, while the second has contributions from both channels. We use the models shown in Fig. 7(b) to calibrate the signal and extract the relative yield from the experiments, which gives a yield of $40\% \pm 5\%$ for the slow channel (more information in Appendix I). The presence of the fast channel could indicate that both channels are present after the IR + UV excitation, or it could originate from molecules that are only excited by the UV and not the IR pulse as a result of imperfect spatial overlap between the laser pulses on the sample.

V. DISCUSSION

In the previous sections, we have clearly demonstrated the capability to carry out a GUED experiment with a pair of time-delayed pump laser pulses, and that the presence of the IR pre-excitation alters the reaction dynamics significantly. The IR pre-excitation opens a dissociation channel through a region of the PES where the potential gradient is small compared to the A-band states, as evidenced by the lower dissociation speed.

We now discuss possible mechanisms by which the IR pre-excitation can alter the dynamics. We believe the most likely mechanism is that vibrational pre-excitation of the molecule through ISRS [57–59] results in the UV pump pulse populating a different excited state, or a different region of the PES where the slope of the potential is less steep and thus the fragments separate more slowly. The bandwidth of our femtosecond laser pulse is sufficient to drive ISRS in the lower energy vibrational modes of CF_3I . Previous experiments on vibrationally mediated photodissociation (VMP) have shown that pre-excitation can lead to dissociation pathways and influence the energy of the fragments [64]. In these experiments, a laser first prepares the molecules to a vibrationally excited state through resonance [65–71] or stimulated Raman excitation [57–59] in the electronic ground state, and subsequently a second laser transfers the population from the ground state to an electronic excited state that is dissociative. Interestingly, we have not found an example of VMP where the pre-excitation leads to a slower dissociation speed, although previous measurements have captured only the final energies and not the dissociation dynamics. A different excited state, involving different parts of the PES, could be reached due to a change in the molecular symmetry or the spread of the wavefunction caused by vibrational excitation. Given that during our measurement time window the C–I bond length is only extended by ~ 1 Å, what we observe may not represent the final speed of the fragments but the first part of the dissociation process where the wave packet moves slowly through a shallow part of the PES. Further studies that capture the final energy of the fragments and *ab initio* calculations will be needed to fully understand this reaction path.

We have also considered two other possible processes that could affect the dissociation dynamics: enhanced two-photon

absorption of the UV laser and ionization by the IR laser through multiphoton absorption. Previous studies have observed that under intense laser conditions, the CF_3I molecule can be excited to a Rydberg state by absorbing two UV photons simultaneously, and that in this state the population is transiently trapped in a higher state before coupling to a dissociative state [3]. The transition dipole for this two-photon excitation, however, is perpendicular to that of the one-photon excitation to the dissociative A band, i.e., it is perpendicular to the molecular axis. Our analysis of the experimental ΔMPDF clearly shows that the dissociation takes place along the C-I axis. Therefore, it is not through the previously observed Rydberg state. In addition, we expect a low probability of multiphoton excitation because the UV laser intensity was 3 times lower than for the experiment of Yang *et al.* where the two-photon excitation to the Rydberg was observed [3].

In the measurements with IR excitation only, we observed no evidence of dissociation or ionization. Dissociation would have produced a clear signature in the diffraction signal, which was not present in the data. Ionization by an intense laser field produces macroscopic electric and magnetic fields that deflect and distort the electron beam [72–74], which we did not observe in the experiment. At the sample density of our experiments, the deflection would have been strong and easily observable. While we cannot completely dismiss the probability of ionization, the fraction of ionized molecules would be too low to account for the different dissociation dynamics observed in the experiment.

VI. CONCLUSIONS

This work extends the existing capacities of GUED to reach unexplored regions of the PES through double excitation, and to capture dynamics in the molecular frame through photoexcitation of aligned molecules. Measurements where a second laser pulse is used to alter the outcome of a reaction triggered by the first laser pulse are also possible, where the reaction would be tracked taking advantage of the real-space sensitivity of GUED. We developed the methodology to carry out experiments with two excitation laser pulses and to analyze and interpret the data, and to retrieve real-space information in the molecular frame. A proof-of-principle experiment shows significantly different dynamics in the UV photodissociation of CF_3I after pre-excitation with an IR femtosecond pulse. We take advantage of the real space and angular resolution of GUED to retrieve the structural changes and directionality of the dissociation. The results show that the IR pre-excitation opens a dissociation channel that traverses a shallower region of the PES.

ACKNOWLEDGMENT

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DATA AVAILABILITY

The data that support the findings of this article are openly available [75].

APPENDIX A: EXPERIMENTAL SETUP

Figure 8 shows a schematic diagram of UED experimental layout. A Ti:sapphire laser generates laser pulses at a wavelength of 800 nm with 7 mJ pulse energy and 50 fs FWHM pulse duration at a repetition rate of 1 kHz. The laser output is split into three beams. Approximately 50% of the IR laser pulse energy is directed to the IR pre-excitation beam, 40% is used to generate a 266-nm pulse to initiate photodissociation of the sample molecules, and 10% to generate another 266-nm pulse for illuminating the photocathode to produce the electron pulses. The two 266-nm UV pulses are generated through frequency tripling of the IR pulses with BBO crystals. Group velocity mismatch between laser and electron pulses has been one major issue that limits keV-GUED to reach a femtosecond temporal resolution [46,47]. In this experiment, the group velocity mismatch is compensated by introducing an angle between the laser and electron beams and by tilting the pulse intensity front of the IR and UV laser pulses with respect to their phase fronts [16,48]. Both the tilted angle of laser pulses and cross angle between the lasers and electron beams are designed to be $\cos^{-1}(v_e/c)$, where v_e and c are speed of electron and laser pulse, respectively. The speed of electrons with a kinetic energy of 90 keV is $0.53 c$, and the cross angle and tilted angle are 58.2° . The inset of Fig. 8 shows a sketch of how the velocity mismatch between electron and laser pulses is compensated at the interaction region using a laser pulse with a tilted intensity front traveling at an angle of 58.2° with respect to the electron beam.

To introduce the tilted angle in the UV laser pulse, we use an aluminum-coated grating with a grating constant of 400 nm and a lens (lens 2 in Fig. 8 with a focal length 230 mm for 266 nm) that images the grating surface to the gas jet with a demagnification factor of 15.2. The incident angle of 6.1° allows the output UV beam to be perpendicular to the surface of grating [76]. We use a gold-coated grating with a constant of 150 nm and a two-lens system that images the grating surface to the gas jet with a demagnification factor of 13.5 to produce the tilted IR pulse. The output IR beam is normal to the surface of grating when the incident angle is 6.9° . The imaging system that consists of two lenses is required for the IR laser since the two lasers are collinear and the imaging relation for the two different wavelengths cannot be obtained using the same lens in the setup. The focal lengths of lens 1 and lens 2 are 2500 and 250 mm for 800 nm. The distance between lens 1 and lens 2 is around 150 mm to obtain an effective focal length of the two-lens system to be 235 mm to serve our purpose.

The electron generation and RF generation and synchronization systems have been described in detail in Ref. [16]. In this experiment, two components in the RF generation and synchronization system reported in Ref. [16] have been updated to improve the phase stability of the 3 GHz time-varying electric field for electron pulse compression. Specifically, the low phase noise amplifier HMC8411LP2FE (AMP2 and

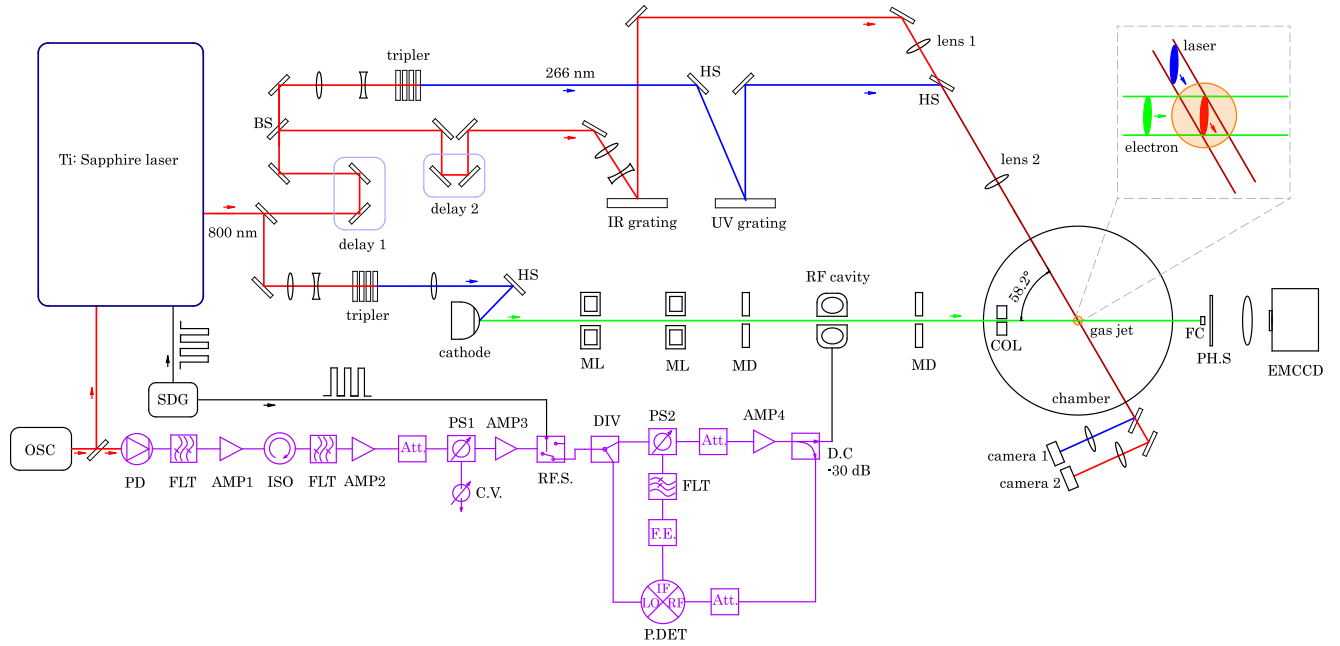


FIG. 8. Diagram of UED experimental setup, not to scale. The paths drawn in red and blue correspond to the 800- and 266-nm wavelength laser beam, respectively. The path drawn in green corresponds to the electron bunch trajectory from the photocathode to the detector. The path in black is the electric 1-kHz trigger signal from the laser control unit (SDG) to control the release timing of laser pulse and 3 GHz pulse. The path in purple corresponds to the 3 GHz RF generation and synchronization system used to drive the RF cavity. The inset shows a sketch of how the velocity mismatch is compensated at the interaction region using a laser pulse with a tilted intensity front travelling at an angle with respect to the electron beam. EMCCD captures the light generated by the diffracted electrons impinging on the phosphor screen. Cameras 1 and 2 are used to monitor the IR and UV laser beams. OSC: oscillator; SDG: signal delay generator; PD: photo diode; FLT: filter; AMP: amplifier; ISO: isolator; Att.: attenuator; R.F.S.: RF switch; DIV: power divider; PS: phase shifter; C.V.: control voltage; F.E.: feedback electronics; P.DET: phase detector; D.C.: directional coupler; ML: magnetic lens; MD: magnetic deflector; COL: collimator; FC: Faraday cup; PH.S: phosphorus screen; BS: beam splitter; HS: harmonic separator.

AMP3 in Fig. 8) and phase shifter HMC928LP5E (PS1) in Ref. [16] have been updated to Holzworth HX2400 and HX5100, respectively.

APPENDIX B: ELECTRON DIFFRACTION THEORY

The total elastic scattering intensity from a single molecule can be written as

$$I(s) = \sum_{j=1}^N \sum_{k=1}^N f_j^*(s) f_k(s) e^{-is \cdot r_{jk}}, \quad (\text{B1})$$

where $f_k(s)$ is the complex scattering amplitude of the k th atom, N is the total number of atoms in the molecule, s is the momentum transfer vector with magnitude $s = \frac{4\pi}{\lambda} \sin(\frac{\theta}{2})$, and r_{jk} is the vector pointing from j th atom to k th atom. The terms in Eq. (B1) where $j = k$ correspond to the atomic scattering intensity, formulated as $I_A(s) = \sum_{k=1}^N |f_k(s)|^2$, while the $j \neq k$ terms, called molecular scattering intensity, represent interference of atomic pairs. Note that s is momentum transfer vector for the 2D diffraction pattern, whereas s is the magnitude of momentum transfer and is used for the 1D scattering intensity. The total scattering intensity I_{total} for a sample of molecules with an anisotropic angular distribution is given by

[16,49]

$$I_{\text{total}}(s) = \iint \sum_{j=1}^n \sum_{k=1}^n f_j^*(s) f_k(s) e^{-is \cdot r_{jk}(\alpha, \beta)} \times g_{jk}(\alpha, \beta) \sin \alpha \, d\alpha d\beta. \quad (\text{B2})$$

When the $g_{jk}(\alpha, \beta)$ only has dependence on α , the diffraction intensity is given by Eq. (1), i.e., in our experiment, linearly polarized lasers are used to pump the molecular ensemble. For a sample of molecules with randomly oriented distribution $g_{jk}(\alpha, \beta) = \frac{1}{4\pi}$, the 2D molecular scattering intensity $I_M(s)$ is given by [77]

$$I_M(s) = \sum_{j=1}^N \sum_{k \neq j}^N f_j^*(s) f_k(s) \frac{\sin(sr_{jk})}{sr_{jk}}. \quad (\text{B3})$$

The molecular scattering intensity $I_M(s)$ can be azimuthally averaged to obtain the 1D scattering intensity $I_M(s)$ with a higher signal-to-noise ratio. Since scattering amplitudes $f_k(s)$ are approximately proportional to s^{-2} , the molecular scattering term $I_M(s)$ decays approximately as s^{-5} . Therefore, the modified scattering intensity is defined to enhance the oscillations in the signal:

$$sM(s) = \frac{sI_M(s)}{I_A(s)}. \quad (\text{B4})$$

In this work, the gas sample is pumped by linearly polarized laser pulses, and $I_M(s)$ does not decay approximately as

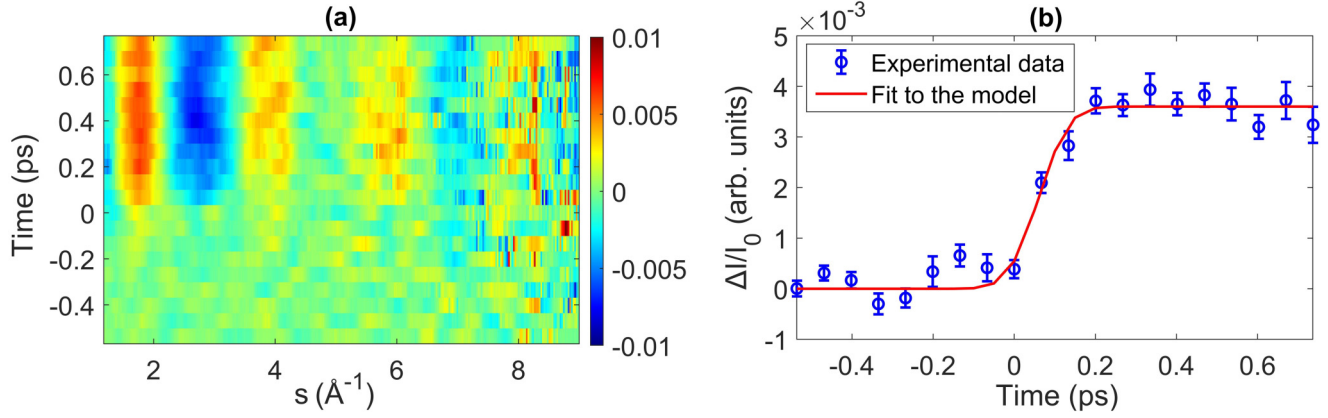


FIG. 9. Temporal resolution characterization using the UV-induced photodissociation dynamics of CF_3I molecules. (a) Fractional difference signal $\Delta I(s, t)/I_0$. (b) The data from 1.3 to 2.1 $\text{\AA}^{-1}$ are integrated to calculate $\Delta I(t)/I_0$ to characterize the instrument response time. The fitting of $\Delta I(t)/I_0$ to the error function model. The experimental data are blue circles, and $h(t)$ with fitted parameters is the red curve. Statistical error bars are generated by bootstrapping at each data point.

s^{-5} . For example, for perfectly aligned molecules given by Eq. (B1), the $I_M(s)$ decays approximately as s^{-4} . Therefore, the 2D modified scattering pattern of anisotropic molecular ensemble here is rescaled as

$$\mathcal{M}(s) = \frac{s^\kappa I_M(s)}{I_A(s)}, \quad (\text{B5})$$

where $0 < \kappa < 1$, and a higher anisotropy corresponds to a smaller κ . It has been shown in Refs. [3, 16, 49] that the atom-pair distances and angular distribution of all atom pairs in real space can be retrieved from the modified pair distribution function. The MPDF is generated by the Fourier inversion, followed by the Abel inversion, of $\mathcal{M}(s)$,

$$\begin{aligned} \text{MPDF}(r, \alpha) &= \text{Abel}^{-1} \text{FT}_{2\text{D}}^{-1}[\mathcal{M}(s)] \\ &= \sum_{j=1}^n \sum_{k=1, j \neq k}^n g_{jk}(\alpha) H(r - r_{jk}) \otimes \frac{\tilde{F}_j(r) \star \tilde{F}_k(r)}{r_{jk}^2}, \end{aligned} \quad (\text{B6})$$

where $0 < \kappa < 1$, $\otimes$ signifies convolution, and $\star$ stands for correlation; $\tilde{F}_j(r)$ is the Fourier transform of the normalized atomic scattering amplitude $f_j(s)/\sqrt{s^{-\kappa} I_A}$; $g_{jk}(\alpha)$ is the angular distribution of atom pair $\mathbf{r}_{jk}$; and $H(r - r_{jk})$ is the convolution of the PDF with the inverse Fourier transform of a function that truncates the diffraction signal to match the limited measurement range. The scattering pattern of a randomly orientated ensemble corresponds to $\kappa = 1$, where scattering pattern with a higher anisotropy corresponds to a smaller κ . The Fourier transform of the normalized atomic scattering amplitude $f_j(s)/\sqrt{s^{-\kappa} I_A}$ is much narrower than that of $f_j(s)$, which is helpful to isolate distances of different atom pairs.

In time-resolved experiments, we use the diffraction-difference method to enhance the change of diffraction pattern, formulated as $\Delta I_M(s, t) = I_{\text{total}}(s, t) - I_{\text{total}}(s, t_0)$, where $I_{\text{total}}(s, t_0)$ is the total scattering intensity at time delay t_0 recorded before the arrival of the laser pulse [17, 50]. The changes in molecular structure and angular distributions can be separated by decomposing $\Delta I_M(s, t)$ into Legendre polynomials, given by Eq. (3). The normalized difference signal is

defined as

$$\mathcal{R}_m(s, t) = \Delta I_{M,m}(s, t)/I_0(s), \quad (\text{B7})$$

where m indicates zeroth- or second-order terms from the Legendre polynomial decomposition, and $I_0(s)$ is the azimuthally averaged $I_{\text{total}}(s, t_0)$. Correspondingly, we can define $\Delta \mathcal{M}(s, t) = s^\kappa \Delta I_M(s, t)/I_A$, and the ΔMPDF is given by

$$\Delta \text{MPDF}(r, \alpha, t) = \text{Abel}^{-1} \text{FT}_{2\text{D}}^{-1}[\Delta \mathcal{M}(s, t)]. \quad (\text{B8})$$

We denote $p(r - r_{ij}) = H(r - r_{jk}) \otimes \frac{\tilde{F}_j(r) \star \tilde{F}_k(r)}{r_{jk}^2}$, and $\text{MPDF} = \sum_{i=1}^N \sum_{j=1, j \neq i}^N g_{ij}(\alpha) p(r - r_{ij})$. The ΔMPDF is given by

$$\begin{aligned} \Delta \text{MPDF} &= \sum_{i=1}^N \sum_{j=1, j \neq i}^N \tilde{g}_{ij}(\alpha) \Delta p(r - r_{ij}) + \Delta g_{ij}(\alpha) p(r - r_{ij}) \\ &= \sum_{i=1}^N \sum_{j=1, j \neq i}^N \Delta g_{ij}(\alpha) \tilde{p}(r - r_{ij}) + g_{ij}(\alpha) \Delta p(r - r_{ij}), \end{aligned} \quad (\text{B9})$$

where $\tilde{p}(r - r_{ij})$ and $\tilde{g}_{ij}(\alpha)$ are the newly produced atom-pair distance and angular distribution of $\mathbf{r}_{ij}$ after the arrival of laser, whereas $g_{ij}(\alpha)$ and $p(r - r_{ij})$ are the terms before arrival of laser, respectively. The changes are given by $\Delta g_{ij}(\alpha) = \tilde{g}_{ij}(\alpha) - g_{ij}(\alpha)$ and $\Delta p(r - r_{ij}) = \tilde{p}(r - r_{ij}) - p(r - r_{ij})$. The ΔMPDF contains direct information on the change of angular distribution $g_{ij}(\alpha)$ and atom-pair distance $p(r - r_{ij})$. When the newly produced atom-pair distances can be isolated from other ones, the $g_{ij}(\alpha)$ can be retrieved from the ΔMPDF .

APPENDIX C: INSTRUMENT RESPONSE FUNCTION

The instrument response time of the keV-GUED is characterized using the diffraction signal produced by the photodissociation of CF_3I with a UV femtosecond laser pulse. The measured instrument response function includes all contributions to the observed temporal resolution: electron and

laser pulse durations, group velocity mismatch, timing jitter, and the intrinsic time of the dissociation process. The C–I bond cleavage in CF₃I molecule upon absorption of one 266-nm photon happens within 50 fs, providing a good metric to estimate the overall temporal resolution of GUED [3,10]. The photodissociation was captured in a series of electron diffraction patterns, denoted by $I_{\text{total}}(s, t)$, as a function of time delay between the UV laser and electron pulses. The time dependent $\Delta I(s, t)/I_0$ is generated with the following steps. First, a background image recorded with no sample is subtracted from all the diffraction images. Second, the 2D diffraction-difference patterns $\Delta I(s, t) = I_{\text{total}}(s, t) - I_{\text{total}}(s, t_0)$ are calculated, where t_0 corresponds to a time before the arrival of the laser pulse, such that the sample is still in the ground state. Third, the $I_{\text{total}}(s, t_0)$ is average azimuthally to obtain $I_0(s)$. Fourth, the diffraction-difference patterns $\Delta I(s, t)$ were divided into four quadrants, corresponding to two vertical and two horizontal cones with an open angle of 90°. This is done because the diffraction signal appears stronger along the direction of laser polarization due to the angular selectivity of the excitation. The diffraction data in the two vertical cones are azimuthally averaged to obtain the $\Delta I(s, t)$. The amplitude of $\Delta I(s, t)/I_0$ calculated from the vertical cones is 2 times larger than that of horizontal cones due to the anisotropy in the diffraction patterns.

The $\Delta I(s, t)/I_0$ is shown in Fig. 9(a). The $\Delta I(s, t)/I_0$ was integrated over the range 1.3–2.1 Å⁻¹ to obtain time-dependent $\Delta I(t)/I_0$ shown in Fig. 9(b). This function represents the rise time of the dissociation signal using the strongest feature in the diffraction pattern. The experimental $\Delta I(t)/I_0$ was shown as the blue circles and the uncertainty was obtained using bootstrapping. An error function is used to fit the data and extract a timescale:

$$h(t) = \frac{c}{2} \left\{ 1 + \operatorname{erf} \left[\frac{2\sqrt{\ln 2}(t - t_0)}{\tau} \right] \right\}, \quad (\text{C1})$$

where $\operatorname{erf}(t)$ is the Gauss error function, τ , c , t_0 are the parameters to fit, and τ characterizes the FWHM temporal resolution of the measurement, which we define as the IRF. The fit returns a value of $\tau = 140 \pm 10$ fs using bootstrapping method, which corresponds to the upper limit of the IRF. The retrieved $h(t)$ is shown by the red curve in Fig. 9(b).

APPENDIX D: NORMALIZED DIFFERENCE SIGNAL

The normalized difference signals for IR-only, UV-only, and IR + UV experiments are calculated with the following steps.

(1) A background image recorded without sample is subtracted from each diffraction image.

(2) The diffraction-difference patterns $\Delta I_M(s, t)$ are calculated by taking the difference between $I_{\text{total}}(s, t)$ and $I_{\text{total}}(s, t_0)$ using Eq. (2), where the variable t denotes the time delay with respect to the laser excitation. For the IR-only and UV-only experiments, the t_0 corresponds to a time delay before the arrival of the pump laser, i.e., before the sample is excited. For the IR + UV experiment, both $I_{\text{total}}(s, t)$ and $I_{\text{total}}(s, t_0)$ are taken at the peak alignment of CF₃I molecules produced by the IR laser, while the $I_{\text{total}}(s, t_0)$ is taken before the arrival of

the UV laser. A diffraction pattern before the arrival of both IR and UV lasers was taken to calculate $I_0(s)$ for the denominator of normalized difference signal, given by Eq. (B7), in IR + UV experiment.

(3) The $\Delta I_M(s, t)$ are decomposed into Legendre polynomials using Eq. (3).

(4) The residual background in $\Delta I_{M,0}(s, t)$ is removed. A third-order polynomial is first fit to the $\Delta I_{M,0}(s, t)$ to approximate the background, and then removed from the signal.

The IR-only excitation produces a very small signal, so in order to extract the amplitude of the signal we averaged the $\mathcal{R}_0(s, t)$ with time delay from -1 to 2.2 ps with a time step of 0.1 ps since the signal plateaus after -1 ps shown in Fig. 2(b). We then performed a 35-point moving average in s to remove high-frequency noise. This produces a time-averaged signal with an amplitude of approximately 0.2%. The signal amplitude is too small to retrieve the signal as a function of time, i.e., at each time step individually. The time-averaged $\mathcal{R}_0(s, t)$ is shown in Fig. 10. The blue shaded area in the figure corresponds to the standard deviation of the measurements obtained by the bootstrapping method.

APPENDIX E: IMPULSIVE ALIGNMENT OF CF₃I MOLECULES

Impulsive alignment of symmetric top molecules by a non-resonant, linearly polarized femtosecond laser is described by the time-dependent Schrödinger equation [54]:

$$i\hbar \frac{\partial \Psi(t)}{\partial t} = H(t)\Psi(t), \quad (\text{E1})$$

$$H_{\text{ind}} = -\frac{1}{4}\mathcal{E}^2(t)\Delta p \cos^2\theta, \quad \Delta p = p_{\parallel} - p_{\perp}, \quad (\text{E2})$$

where $H(t) = H_{\text{rot}} + H_{\text{ind}}$, and $H_{\text{rot}} = C_e \mathbf{J}^2 + (A_e - C_e)J_z^2$ and H_{ind} is the potential energy of the induced dipole in the electric field of the laser; the rotational constants $A_e > C_e$ are for a prolate symmetric top molecule; $\mathcal{E}(t)$ is the envelope of the electric field; $p_{\parallel}$ and $p_{\perp}$ are the polarizability tensor components that are parallel and perpendicular to the molecular axis, respectively; and θ is the angle between molecular axis and the laser polarization direction. Equation (E1) can be solved numerically using the symmetric top eigenfunctions $|JKM\rangle$ as basis functions [78], with

$$|JKM\rangle = \left(\frac{2J+1}{8\pi^2} \right)^{\frac{1}{2}} e^{iM\phi} d_{MK}^J(\theta) e^{iK\chi}, \quad (\text{E3})$$

where $d_{MK}^J(\theta)$ is the Wigner's d matrix and (ϕ, θ, χ) are the Euler angles. The interaction of a linearly polarized laser field with a symmetric top molecule does not alter the quantum numbers K and M [54]. Therefore, the wave packet can be expanded as $\Psi_{J,K_i,M_i}(t) = \sum_J c^{J,K_i,M_i}(t) |JK_iM_i\rangle$, where $|JK_iM_i\rangle$ are the initial states in an ensemble governed by the Boltzmann distribution $W_{J,K_i,M_i}(T)$ with a nuclear spin statistics weight [79], and T is the temperature of the ensemble. The coefficients $c^{J,K_i,M_i}(t)$ are calculated numerically. The degree of alignment, which is commonly used to describe the evolution

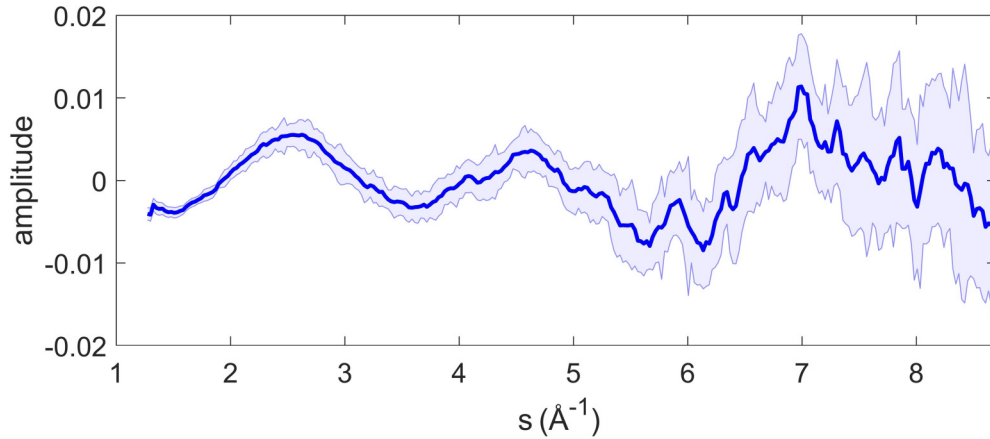


FIG. 10. Normalized difference signal that indicates structure change of CF₃I due to the IR excitation.

of the alignment, is defined as

$$\langle \cos^2 \theta \rangle(t) = \sum_{J_i, K_i, M_i} W_{J_i K_i M_i}(T) \langle \Psi_{J_i K_i M_i}(t) | \cos^2 \theta | \Psi_{J_i K_i M_i}(t) \rangle. \quad (\text{E4})$$

The probability density of the aligned molecules is given by $\rho = \sum_{J_i, K_i, M_i} W_{J_i K_i M_i}(T) |\Psi_{J_i K_i M_i}(t)|^2$. In the case of symmetric top molecules aligned by a linearly polarized laser field, the probability density can be written as $\rho(\phi, \theta, \chi, t) = (\frac{1}{2\pi})^2 \rho_1(\theta, t)$ since it has no dependence on ϕ and χ . With the geometrical structure of the molecule and $\rho_1(\theta, t)$, the scattering pattern $I_M(s, t)$ can be calculated with the method described in Ref. [60]. The time-dependent anisotropy signal $u_2(t)$ shown in Fig. 2(c) can be calculated using $u_2(t) = \int_{2.3}^{3.2} \mathcal{R}_2(s, t) ds$. The temperature of the sample is not known accurately *a priori*, so it is determined by comparing the experimental and theoretical $u_2(t)$ using the fitting method described in Ref. [49].

APPENDIX F: EXPERIMENTAL Δ MPDF

In this Appendix, we describe the procedure to retrieve the experimental Δ MPDF.

(1) We start from the $\Delta I_M(s, t) = I_{\text{total}}(s, t) - I_{\text{total}}(s, t_0)$ as described in Appendix D.

(2) The $\Delta I_M(s, t)$ are projected onto Legendre polynomials using Eq. (3).

(3) The residual background in the $\Delta I_M(s, t)$ is corrected using a third-order polynomial that is first fitted and then subtracted from the $\Delta I_M(s, t)$.

(4) The region of missing data at low s (due to the beam stop) is smoothly interpolated to zero at the center of the pattern from the surrounding values [17,26].

(5) The $\Delta \mathcal{M}(s)$ is calculated using Eq. (B5) and a Gaussian damping term $e^{-0.025 \times s^2}$ is applied to suppress the noise and artifacts at higher s values where the SNR is lower [51].

(6) The Δ MPDF is calculated using Eq. (4) using a momentum transfer range up to $s = 9.2 \text{ \AA}^{-1}$ and the zero-padding technique is applied in $\Delta \mathcal{M}(s)$ to decrease the step size of the Δ MPDF.

The calculations of the Δ MPDF and the Δ PDF_{||} are outlined graphically in Fig. 11. The $\Delta \mathcal{M}(s)$ in the IR + UV experiment at $t = 0.4 \text{ ps}$ is shown in Fig. 11(a). The polarization of both IR and UV lasers is along the y axis in Fig. 11(a). An obvious anisotropy imprints in the diffraction pattern. The data inside of the black circle ($s < 1.17 \text{ \AA}^{-1}$) are

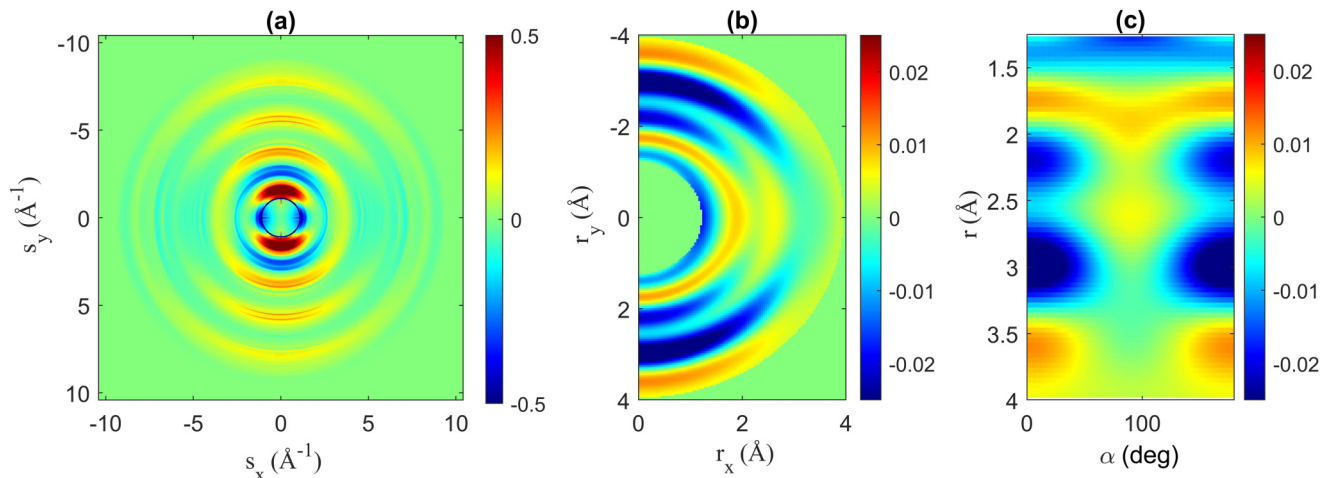


FIG. 11. (a) $\Delta \mathcal{M}(s)$ for the IR + UV excitation. The data inside of the black circle, corresponding to the missing data due to beam stop, are interpolated smoothly to zero at the center of the pattern. (b) Δ MPDF(r_x, r_y). (c) Polar representation of Δ MPDF(r, α).

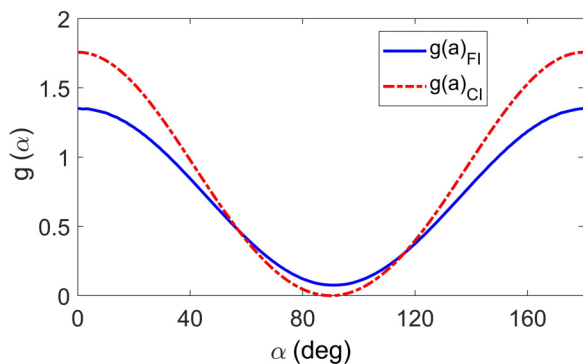


FIG. 12. The angular distribution of atom pair F-I, shown by the blue curve, is measured experimentally. The retrieved angular distribution of C-I is the red dash curve. Angular distribution of C-I is the orientation distribution of CF_3I molecules.

not accessible experimentally due to the presence of the beam stop that stops the directly transmitted electron beam. The missing data are filling in by extrapolating the data outside the region to zero at the center of the pattern.

The experimental ΔMPDF for $t = 0.4$ ps is shown in Fig. 11(b). The dashed lines correspond to the interatomic distances of the ground-state CF_3I : $r_{\text{CF}} = 1.33$ Å, $r_{\text{CI}} = 2.14$ Å, $r_{\text{FF}} = 2.15$ Å, and $r_{\text{FI}} = 2.89$ Å. The depletion signals of ground-state F-I and C-I distances show a stronger signal along the vertical direction due to the selectivity of the photoexcitation where the excitation probability is highest for molecules aligned along the direction of laser polarization. The projection of the dissociation wave packet onto the F-I distance can be clearly identified by the positive signal around 4 Å at $t = 0.4$ ps. The signal of F-F distance, described by the positive region around $r_{\text{FF}} = 2.15$ Å that appears preferentially perpendicular to the y axis, indicates the hot vibrational motion of the CF_3 fragment. The signal of C-F is subjected to artifacts due to the interpolation of the missing data and residual background correction in the experimental pattern, which will be discussed in Appendix H. The ΔMPDF of aligned molecules provides information about the structural dynamics in the molecular frame.

Figure 11(c) shows the ΔMPDF in polar representation, in which both the internuclear distances and angular distribution of atom pairs can be clearly identified and be extracted. We focus on the structural changes along the polarization direction by integrating the signal over an angular range from 0° to 10° to generate the $\Delta\text{PDF}_{\parallel}$. This function captures the signal of the C-I bond elongation dynamics primarily in the F-I interference signal that has a stronger signal than the C-I (there are three F-I distances that contribute to the signal and only one C-I distance). The $\Delta\text{PDF}_{\parallel}(r, t)$ shown in Fig. 6 was calculated over the range of -0.1 to 0.45 ps.

The angular distribution of C-I of CF_3I molecules is required to calculate the diffraction patterns using the simple mode of dissociation. Here, we extracted the angular distribution of F-I from the ΔMPDF in polar representation, which is used to retrieve the angular distribution of C-I. In our experiment, the CF_3I molecules are impulsively aligned with the IR laser and subsequently are triggered by the UV laser. Part of the aligned CF_3I molecules are excited by the UV laser to initiate dissociation. The $1/e$ rotational dephasing timescale of the parent CF_3I molecule is 1.5 ps, which is evaluated in Ref. [3] based on a free-jet expansion model [80]. For molecules with larger moments of inertia, the dephasing time is longer. Therefore, the orientation distribution of parent CF_3I molecules, and product $\text{CF}_3\text{-I}$ molecules with an extended C-I distance, are approximately fixed during the photodissociation over a temporal window of ~ 0.5 ps. In the experimental ΔMPDF , the F-I distance can be clearly isolated from other atom pairs. Now, we can focus on the signal of F-I pair to extract its angular distribution using Eq. (B9). The parent and product molecules are approximated to be not rotating over the measurement window, the change of the angular distribution of atom pair F-I is zero, formulated as $\Delta g_{\text{FI}}(\alpha) = 0$. At $t = 0.4$ ps, the F-I distance is elongated, which is indicated by the positive signal between 3.5 and 4 in Fig. 11(c), and is clearly isolated from the original distance $r_{\text{FI}} = 2.89$ Å. Therefore, distribution of ΔMPDF at $r_{\text{FI}} = 2.89$ Å is given by $-g_{\text{FI}}(\alpha)p(r-2.89 \text{ Å})$. By integrating $-g_{\text{FI}}(\alpha)p(r-2.89 \text{ Å})$ along the r axis around 2.89 Å, we can obtain the unnormalized $g_{\text{FI}}(\alpha)$. The normalized angular distribution of F-I is given by $g_{\text{FI}}(\alpha)/\int_0^\pi g_{\text{FI}}(\alpha) \sin \alpha d\alpha$, and

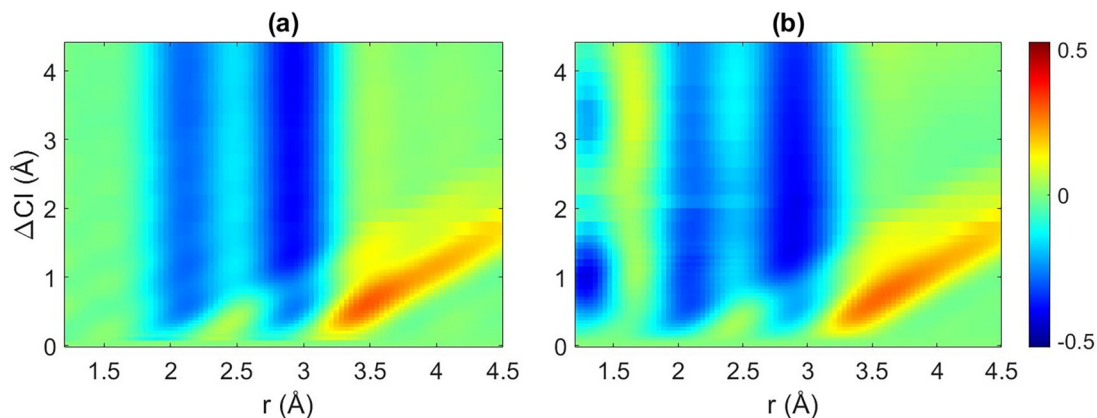


FIG. 13. Simulated $\Delta\text{PDF}_{\parallel}(r, \Delta\text{CI})$. (a) Calculated $\Delta\text{PDF}_{\parallel}$ with only Gauss damping applied. (b) Calculated $\Delta\text{PDF}_{\parallel}$ with the same treatment of the experimental data applied to the simulated $\Delta\mathcal{M}(s, t)$.

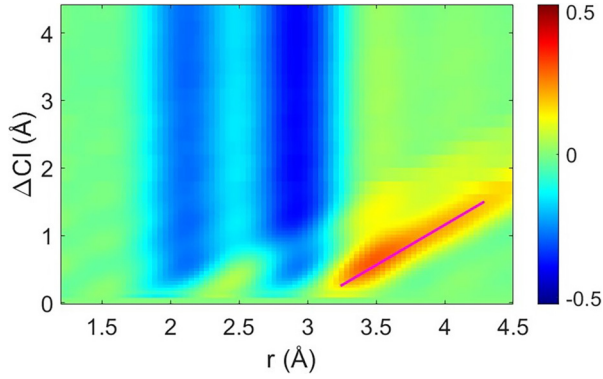


FIG. 14. Simulated $\Delta\text{PDF}_{||}(r, \Delta\text{CI})$ based on the simple model. The peak positions of F–I signal at all ΔCI are obtained and fitted to a linear function. The fitted slope is 1.19 ± 0.04 , and the red line is the linear function with fitted parameters.

is shown as blue line in Fig. 12. The C–I angular distribution $g_{CI}(\alpha)$, which is orientation distribution of CF_3I molecules (shown as the red dash line in Fig. 12), is retrieved using the method described in Ref. [49].

APPENDIX G: CF_3I A-BAND EXCITATION

The UV absorption of CF_3I in the A band consists of three repulsive states overlapped in energy denoted as $^3\text{Q}_1$, $^3\text{Q}_0$, and $^1\text{Q}_1$, involving promotion of a nonbonding (n) electron from the iodine atom valence shell to the σ^* antibonding orbital of the C–I bond. The repulsive potential energy surfaces result in a prompt cleavage of the C–I bond [36–43] to produce excited and ground-state iodine atoms. The $^3\text{Q}_0$ state excitation involves a transition dipole moment parallel to the C–I bond, and the corresponding photodissociation product is the spin-orbit excited state iodine $\text{I}^*(^2\text{P}_{1/2})$ [42,81,82]. The transition dipole moments for excitation of the $^3\text{Q}_1$ and $^1\text{Q}_1$ states are perpendicular to the C–I bond, producing ground-state iodine $\text{I}(^2\text{P}_{3/2})$ [42,81,82]. Ground-state $\text{I}(^2\text{P}_{3/2})$ can also be generated by the nonadiabatic coupling of the $^3\text{Q}_0$ and $^1\text{Q}_1$ states [41,81]. The reported quantum yield of $\text{I}^*(^2\text{P}_{1/2})$ upon A-band excitation is ~ 0.9 , which is almost 1 order of magnitude larger than the yield of $\text{I}(^2\text{P}_{3/2})$ [38,63]. Therefore,

the signal measured by GUED is mostly contributed from the dissociation channel that produces $\text{I}^*(^2\text{P}_{1/2})$. The energy to break C–I bond of CF_3I to produce $\text{CF}_3 + \text{I}^*(^2\text{P}_{1/2})$ is 2.5 eV, and to produce $\text{CF}_3 + \text{I}(^2\text{P}_{3/2})$ is 3.5 eV [43].

APPENDIX H: DIFFRACTION PATTERN SIMULATION AND MAPPING DISTANCE TO TIME

We use a simple model to simulate the dissociation process (the model is described in Sec. IV C) to validate our interpretation of the $\Delta\text{PDF}_{||}$ signal that captures the dissociation dynamics. In order to simulate the MPDF, the orientation distribution of the ensemble of excited CF_3I molecules $g_{CI}(\alpha)$ is needed. This was determined in Appendix F for the case of IR + UV excitation. For the UV-only case, the $g_{CI}(\alpha)$ is assumed to be $\frac{2}{\pi} \cos^2 \alpha$ [3,51]. We use the fast calculation algorithm described in Ref. [60] to calculate the diffraction pattern for a series of different values of ΔCI from 0 to 15 Å. The difference pattern is calculated as a function of the distance change, $\Delta I_M = I_M(s, \Delta\text{CI}) - I_M(s, \Delta\text{CI} = 0)$.

The limitations of the experimental data, specifically the missing data at low s values and residual background can potentially introduce artifacts in the $\Delta\text{PDF}_{||}$. We use our simulations not only to compare with the experimental data but also to carefully check whether the data analysis introduces artifacts. Here, we compare the $\Delta\text{PDF}_{||}$ of the simulated diffraction patterns in two cases. The first case is that we only apply the Gauss damping to simulated $\Delta\mathcal{M}(s)$ and subsequently calculate the ΔMPDF and $\Delta\text{PDF}_{||}$. The second case is that we apply the same procedures used in the experimental data analysis, including the interpolation of missing data region, background correction, and Gauss damping, to calculate the ΔMPDF and $\Delta\text{PDF}_{||}$. The calculated $\Delta\text{PDF}_{||}$ for the first and second cases are shown in Figs. 13(a) and 13(b), respectively. The comparison shows that artifacts appear in the $\Delta\text{PDF}_{||}$ for $r \leq 1.50$ Å due to the background correction and the interpolation of missing data. However, the features of the $\Delta\text{PDF}_{||}$ that we use for our analysis are all at $r < 1.50$ Å, where the signal is not affected. Therefore, we expect the signal of C–I and F–I elongation to be retrieved accurately.

The next step is to convert the ΔCI to time for comparing with the experimental data. For this, we use the dissociation

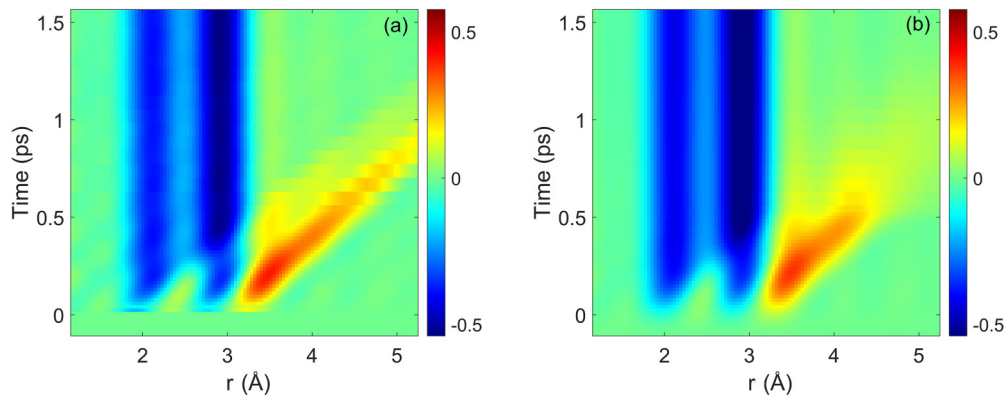


FIG. 15. Simulated $\Delta\text{PDF}_{||}(r, t)$ for IR + UV excitation: (a) without convolution and (b) convolving with a Gaussian function with an FWHM width of 150 fs that reflects the IRF.

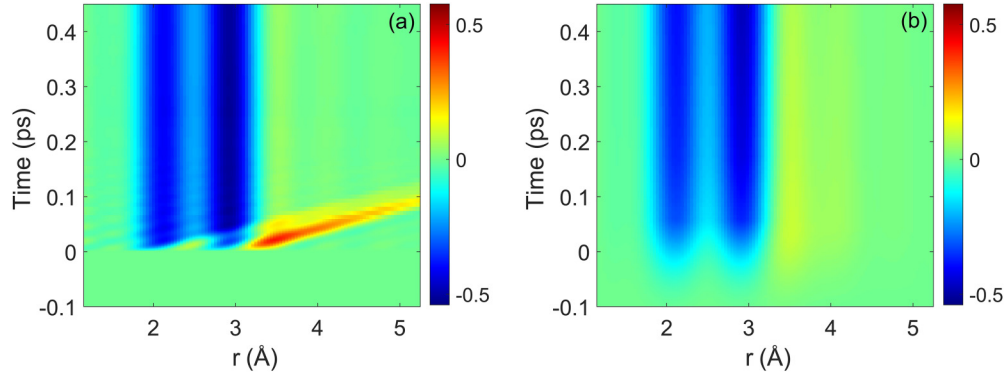


FIG. 16. Simulated $\Delta\text{PDF}_{||}(r, t)$ for UV-only excitation: (a) without convolution and (b) convolving with a Gaussian function with an FWHM width of 150 fs that reflects the IRF.

speed extracted from the experimental $\Delta\text{PDF}_{||}$ for the IR + UV case, and for the UV-only excitation we use a value of the speed from the literature. The experimental $\Delta\text{PDF}_{||}(r, t)$ for the IR + UV experiments is shown in Fig. 6(b). The changing F–I distance, indicated by the positive tilted signal, can be clearly identified and used to extract the relative speed of the fragments. We first retrieve the peak position of the F–I signal at each time delay. We then use a linear fit to extract the speed of the moving wave packet, which gives a value of 2.37 ± 0.23 Å/ps. The simulated $\Delta\text{PDF}_{||}$ based on the simple model is a function of ΔCI , shown in Fig. 14.

For IR + UV excitation, we converted the ΔCI (vertical axis of Fig. 14) to time (ps) by comparing the slope of the tilted F–I signal in the experimental $\Delta\text{PDF}_{||}(r, t)$ to the counterpart in the simulated $\Delta\text{PDF}_{||}(r, \Delta\text{CI})$ shown in Fig. 14. The peak positions of F–I signal at all ΔCI are obtained in unit of Å, which are fitted to a linear function to obtain the slope of the tilted F–I signal. The fitted slope is 1.19 ± 0.04 , and the red line in Fig. 14 is the linear function with fitted parameters. Therefore, the ratio of converting ΔCI (Å) to time (ps) is 2.82 ± 0.29 Å/ps, which is the rate of C–I elongation, called dissociation speed in the main text.

After converting the simulated $\Delta\text{PDF}_{||}$ to time, it is convolved with a Gaussian function with an FWHM (150 fs) to match the IRF of the experiment. The calculated $\Delta\text{PDF}_{||}$ without convolution is shown in Fig. 15(a), and it is shown after the convolution in Figs. 15(b) and 7(b). The convolution affects mostly the data at early times and smears the positive peak from the dissociation wave packet.

We also applied the same procedure to simulate $\Delta\text{PDF}_{||}$ for the UV-only experiment. We used a dissociation speed of 22.51 Å/ps retrieved from the *ab initio* calculation for one UV photon excitation of CF_3I reported in Ref. [3]. The calculated $\Delta\text{PDF}_{||}$ without and with convolution for UV excitation are shown in Figs. 16(a) and 16(b). Here, because of the higher speed of dissociation, the convolution completely blurs out the positive signal from the dissociating wave packet.

APPENDIX I: COMBINATION OF FAST AND SLOW SIGNALS

The data for the IR + UV excitation shown in Fig. 6(b) are best matched by a combination of fast and slow channels.

This is quantified by calculating the ratio (absolute value) of the amplitude of the tilted F–I distribution and F–I depletion signal, and comparing the ratios obtained from Figs. 6(b) and 7(b) that correspond to signal of 100% slow reaction channel to estimate the relative yield of the two channels. For example, the ratio of the amplitude of the tilted F–I distribution to F–I depletion signal in Fig. 6(b) at $t = 0.3$ ps is 0.32, whereas the ratio at the same time delay is 0.84 obtained from Fig. 7(b). Therefore, the yield of the slow reaction channel is 0.37 by comparing the signals at $t = 0.3$ ps. We compared the ratios obtained from Figs. 6(b) and 7(b) from 0.2 to 0.4 ps, and the relative yield of the slow reaction channel is estimated to be 0.40 ± 0.05 . The relative yield of the slow reaction channel is estimated to be 0.4, and that of the fast reaction channel is 0.6. Therefore, the total signal that contains both the slow and fast reaction channels is given by $0.4 \times \Delta\text{PDF}_{||}^{\text{slow}} + 0.6 \times \Delta\text{PDF}_{||}^{\text{fast}}$, where $\Delta\text{PDF}_{||}^{\text{fast}}$ and $\Delta\text{PDF}_{||}^{\text{slow}}$ are shown in Figs. 7(a) and 7(b). The total signal, which is shown in Fig. 17, matches the signal amplitude of experimental result in Fig. 6(b). However, since the simple model does not consider the vibrational motion of CF_3 , the early dynamics in modeled total signal shown in Fig. 17 do not resemble the counterpart in experimental result.

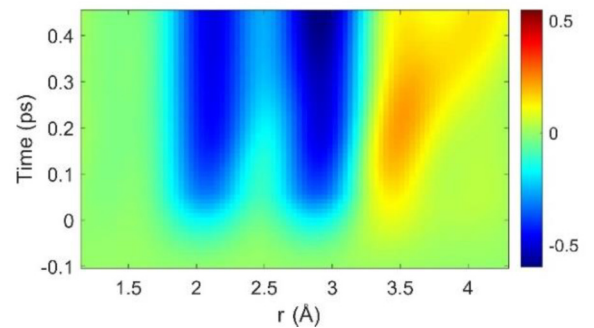


FIG. 17. The total signal contains both the slow and fast reaction channels.

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