# Angular distributions of $CH_3I$ fragment ions under the irradiation of a single pulse and trains of ultrashort laser pulses*

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The angular distribution of $CH_3I$ is investigated experimentally using a single Fourier transform-limited laser pulse and a pulse train, where a 90-fs 800-nm linearly polarized laser field with a moderate intensity of $2.8\times10^{13}$ W/cm$^2$ is used. The dynamic alignment is demonstrated in a single pulse experiment. Moreover, a pulse train is used to optimize the molecular alignment, and the alignment degree is almost identical to that with the single pulse. The results are analysed by using chirped femtosecond laser pulses, and it demonstrates that the structure of pulse train rather than its effective duration is crucial to the molecular alignment.

**Keywords:** shaped femtosecond pulse, molecular alignment, angular distribution

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## 1. Introduction

The study of molecular alignment resulting from the interaction of molecules with laser fields has attracted a lot of attention because of its widespread applications, such as chemical reaction dynamics,[1] high-order harmonic generation,[2] double ionization,[3] and nonsequential double ionization.[4] In a number of studies, it was shown that molecules can be aligned by a continuous laser field as well as a pulsed laser field.[5,6] Dynamic and geometric alignment mechanisms have been used to interpret the observed anisotropic angular distributions of ionic fragments under different experimental conditions.[7–9] In the geometric alignment mechanism, the angular distribution of the fragments is determined by an ionization rate, which is dependent on the angle between the laser polarization vector and the molecular axis. In the dynamic alignment mechanism, because the electric field of the intense laser interacts with the dipole moment of the molecule, which is induced by the laser, this leads to a torque aligning the molecule along the laser polarization. With long laser pulses, the torque is enough to cause an adiabatic alignment.[10] However, with ultrafast pulses, the torque provides an instantaneous kick toward alignment,[11] and a strong enhancement of the alignment occurs after the pulses have been turned off.[12] The molecular nonadiabatic alignment degree is affected by some factors, including the pulse duration,[13] and the highest occupied molecular orbital,[14] etc.

There is a limit to the degree of alignment that can be attained with a single Fourier transform-limited (TL) laser pulse. The degree of molecular alignment can be characterized by an alignment factor, which is $A_{\min} \approx 0.075$ for a TL pulse.[15] In order to achieve an enhanced molecular alignment beyond this limit, many groups have tried to use more complex pulse shapes. In a number of studies, it was shown that two pulses,[16,17] and a train of pulses which are designed based on theoretical research[18] can be used for molecular alignment. More recently, research effort has been devoted to studying molecular alignment using pulse shaping techniques.[19–21]

In the present paper, spectral phase modulated femtosecond laser pulses are used to optimize molecular alignment. We first study angular distributions of $CH_3I$ irradiated by a single ultrashort laser pulse with a moderate intensity ranging from $1.45\times10^{13}$ W/cm$^2$ to $3.15\times10^{13}$ W/cm$^2$. The alignment mechanism is determined by the ratio of fragment yield with laser polarization parallel to the time-of-flight axis to that with laser polarization perpendicular to the time-of-flight axis. The results indicate that the dynamic alignment mechanism dominates under the experimental conditions. Then the molecular alignment is optimized by using a train of ultrashort laser pulses. The mechanisms are analysed using chirped laser pulses. The results demonstrate that the structure of the pulse-train rather than the effective duration of the pulse is crucial to optimizing the alignment in our experiment.

## 2. Experimental setup

The experimental setup used to study molecular alignment in our experiment has been described elsewhere.[22,23] Briefly, the laser system is a Ti:sapphire chirped-pulse amplification laser (Spectra-Physics Tsunami oscillator and Spitfire amplifier) with a central wavelength of 800 nm, a pulse duration of 90 fs, and a repetition rate of 1000 Hz. The laser beam is focused by a lens with a focal length of 225 mm into a vacuum chamber to interact with the $CH_3I$ molecules. A half-wave plate and a Glan prism are placed in front of the

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lens for the purpose of varying the laser intensity continuously. Another half-wave plate between the Glan prim and the lens is used to change the polarization direction. The commercial methyl iodide of 98% purity, available from Tianjin Guangfu Fine Chemical Research Institute, is directly used without further purification. The sample is ejected continuously under a pressure of 55 kPa through an orifice of diameter 21 μm into the vacuum chamber of background pressure $1\times10^{-5}$ pa. In our experimental setup, the polarization angle is defined as the angle between the detection axis of the time-of-flight (TOF) and the polarization vector of the laser light. Here, horizontal and vertical polarizations refer to the polarizations parallel and perpendicular to the detection axis of the TOF, respectively. The produced ions in the femtosecond laser field are collected by a dual micro-channel plate (MCP) detector at the end of the flight tube, and the detected signal is amplified by a preamplifier (ORTEC vt120) and sent to a picosecond time analyzer (EG&G 9308) or oscilloscope (Tektronix TDS 3054B). Then the data are sent to a computer.

The pulse shaping technique in the present work is similar to that used in our previous work, in which the open-loop optimization[24] and the closed-loop optimization[25] are used to control the photoluminescence of gallium arsenide. The pulses are shaped by a 640 pixel dual-mask spatial light modulator (SLM) (CRI Inc., SLM-640), using a standard four-time focal-length configuration to disperse the laser beam and image it onto the SLM and then to recompose and recollimate the shaped beam. A pair of cylindrical lenses ($f = 300$ mm) and gratings (2000 grooves/mm) are used for spectrally dispersing (at the input) and recollimating (at the output) the laser pulses. A sine phase function is applied to the SLM to produce a pulse train that is described in detail elsewhere.[24] A train of three equally spaced femtoscond laser pulses is used to align the $CH_3I$ molecules. A quadratic phase function is used to produce the chirped pulses.

## 3. Results and discussion

### 3.1. Fragment angular distributions with a TL pulse

The laser propagation direction, molecular beam direction, and ion flight direction are perpendicular to each other. The ion intensity angular distribution is measured by changing the relative angle between the laser polarization and the TOF axis. The angular distributions of $I^{a+}$ ($a = 1, 2, 3$), $CH_b^+$ ($b = 1, 2, 3$), and $C^+$ from $CH_3I$ are shown in Fig. 1. All ion distributions exhibit a similar appearance. The maximum yield occurs in the direction parallel to polarization, and the minimum yield occurs in the direction perpendicular to polarization. The full widths at half maximum of $I^{a+}$ with $a = 1, 2$, and 3 are approximately 96°, 104°, and 96, respectively. For $CH_b^+$ ($b = 1, 2, 3$) and $C^+$, the full widths at half maximum are almost equal, which are all approximately 56°.

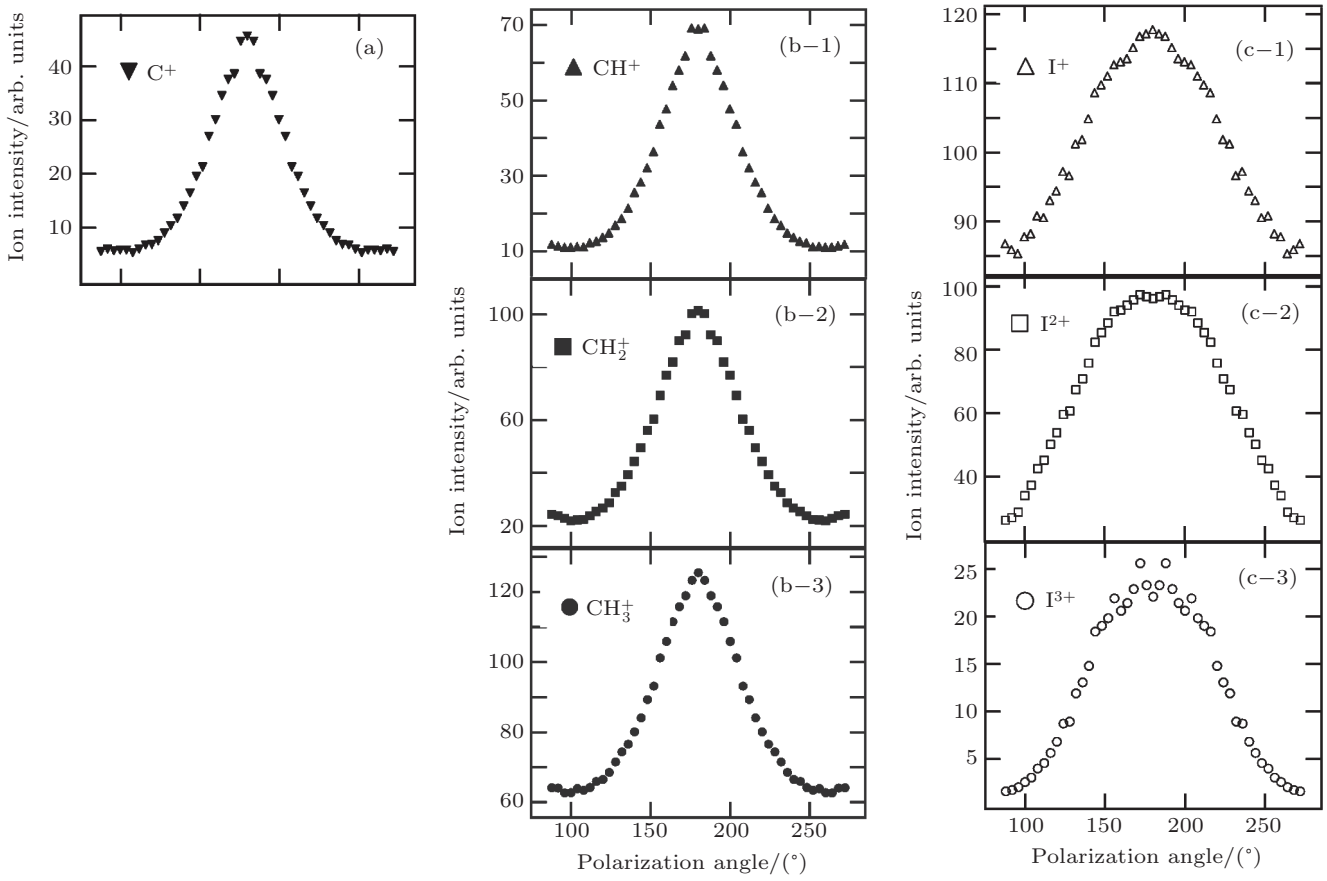



**Fig. 1.** Angular distributions of (a) $C^+$, (b) $CH_b^+$ ($b = 1$–3), and (c) $I^{a+}$ ($a = 1, 2, 3$) with a 800 nm, 90 fs laser at an intensity of $2.8\times10^{13}$ W/cm$^2$.

Further experiments are carried out to elucidate the alignment mechanism. One of them is to measure the ratio of fragment ion yield obtained at the horizontal polarization to that obtained at the vertical polarization, $S_{\rm Para}/S_{\rm Perp}$, within a range of laser intensities.[26] If the ratio decreases with increasing laser intensity, the geometric alignment is responsible for the anisotropic angular distribution of the exploding fragments. Conversely, the dynamic alignment is dominant. As shown in Fig. 2, the intensity ratios of both $CH_3^+$ and $I^+$ fragments, i.e., the values of $S_{\rm Para}/S_{\rm Perp}$, increase with increasing laser intensity in the range from $1.45\times10^{13}$ W/cm$^2$ to $3.15\times10^{13}$ W/cm$^2$, which is a proof of the dynamic alignment.

The angular distributions of product ions arising from the laser fragmentation of $CH_3I$ molecules have been studied using different duration pulses by other groups.[7,9,10] Graham *et al.*[9] and Ma *et al.*[7] demonstrated that the geometric alignment is the dominant mechanism for $CH_3I$ irradiated by laser pulses of intensities $10^{16}$ W/cm$^2$ and $10^{15}$ W/cm$^2$ and durations 50 fs and 110 fs, respectively. Kaziannis *et al.*[10] demonstrated the dynamic alignment mechanism for $CH_3I$ under a long laser pulse (35 ps) of intensity $10^{15}$ W/cm$^2$. However, the dynamic alignment is the dominant mechanism in our experiment in which a short laser pulse (90 fs) is used. Because the laser intensity, which is $2.8\times10^{13}$ W/cm$^2$ in our experiment, is much smaller than that of Ma *et al.*,[7] it is reasonable to assume that our alignment mechanism is different from that given by Ma *et al.* The dynamic alignments of $C_2H_4$ and CO molecules have been demonstrated with two 110 fs linearly polarized laser pulses with perpendicular polarizations by Xu *et al.*[27] and Jiang *et al.*[28] The alignment mechanism of $CH_3I$ in the present experiment could be that the rising edge of the laser pulse aligns the molecules along the laser polarization direction prior to ionization, thereby resulting in the anisotropic angular distribution of the exploding fragments.

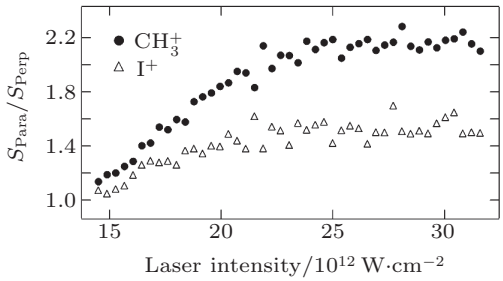



**Fig. 2.** Ratios $S_{\rm Para}/S_{\rm Perp}$ of $CH_3^+$ and $I^+$ versus laser intensity, where $S_{\rm Para}$ and $S_{\rm Perp}$ are the intensities recorded at 800 nm with parallel and perpendicular polarizations, respectively.

### 3.2. Optimizing molecular alignment with a train of laser pulses

A sequence of evenly spaced pulses is generated by using the sine phase function

$$\psi(\omega) = A\sin\left[(\omega-\omega_{\rm ref})T+\phi\right], \tag{1}$$

where $\psi(\omega)$ is the phase applied to the $\omega$ frequency component, and $\omega_{\rm ref}$ is a reference frequency. The amplitude $A$ determines the number of pulses in the train, $T$ determines the spacing between them, and $\phi$ is a constant phase offset.[24] In order to select a pulse train that can be used to optimize molecule alignment, we study the effect of pulse separation in the train on the ratio of ion intensity at the parallel polarization to that at the perpendicular polarization. In this experiment, $A$ is chosen to be 1.2566 to generate a three-pulse train, $\phi$ is fixed at 0, and $T$ is scanned from 10.25 to 151.226, which corresponds to a pulse separation from 1.78 ps to 120 fs. The ion yields of $I^+$ and $CH_3^+$ increase with the increasing pulse separation for different polarizations, shown in Fig. 3. A prominent peak is observed at the pulse separation of 200 fs for both cases of $CH_3^+$ and $I^+$.

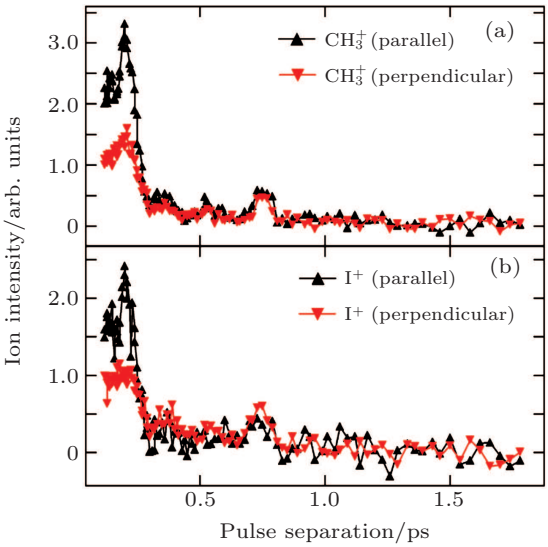



**Fig. 3.** (color online) (a) $CH_3^+$ and (b) $I^+$ intensities versus pulse separation in the train for two different polarization directions.

The molecular alignment degree can be approximately expressed by using the ratio of ion intensity at the parallel polarization to that at the perpendicular polarization. The ratio becomes larger with the increase of molecular alignment degree. For $CH_3^+$ and $I^+$, their intensity ratios reach maxima when the pulse separation is 200 fs where the peak is observed in Fig. 3. The ratios between $CH_3^+$ peak intensities and between $I^+$ peak intensities are 2.55 and 2.44, respectively. From the above analysis, we choose the pulse train with a pulse separation of 200 fs to optimize the molecular alignment in the following experiment.

The relative angle between laser polarization and the TOF axis is scanned, and the ion fragment angular distributions of $CH_3I$ corresponding to a single pulse and a pulse train are compared. The parent ion distribution is characteristically isotropic and is not shown. In Fig. 4, the intensities of $I^+$, $I^{2+}$, $CH_3^+$, and $CH_2^+$ fragment ions obtained with the pulse train are larger than those obtained with the single pulse except around 90° and 270°. For $C^+$ and $CH^+$, their yields under the action of the pulse train do not obviously increase compared with that under the action of the single pulse. The intensities of $I^+$, $I^{2+}$, $CH_3^+$, and $CH_2^+$ fragment ions are enhanced, and the possible reason for this is that the ionization is enhanced as the fragments each reach a critical internuclear separation, which is proposed by Cardoza *et al*.[29] They maximized the $CF_3^+/CH_3^+$ production ratio in the dissociative ionization of $CH_3COCF_3$ by using a closed-loop learning control. The $CF_3$ ionization probability as a function of C–$CF_3$ bond length is calculated using quasistatic tunneling and enhanced ionization theory, and the result is that the ionization probability reaches a maximum at the internuclear separation of 3.6 Å.

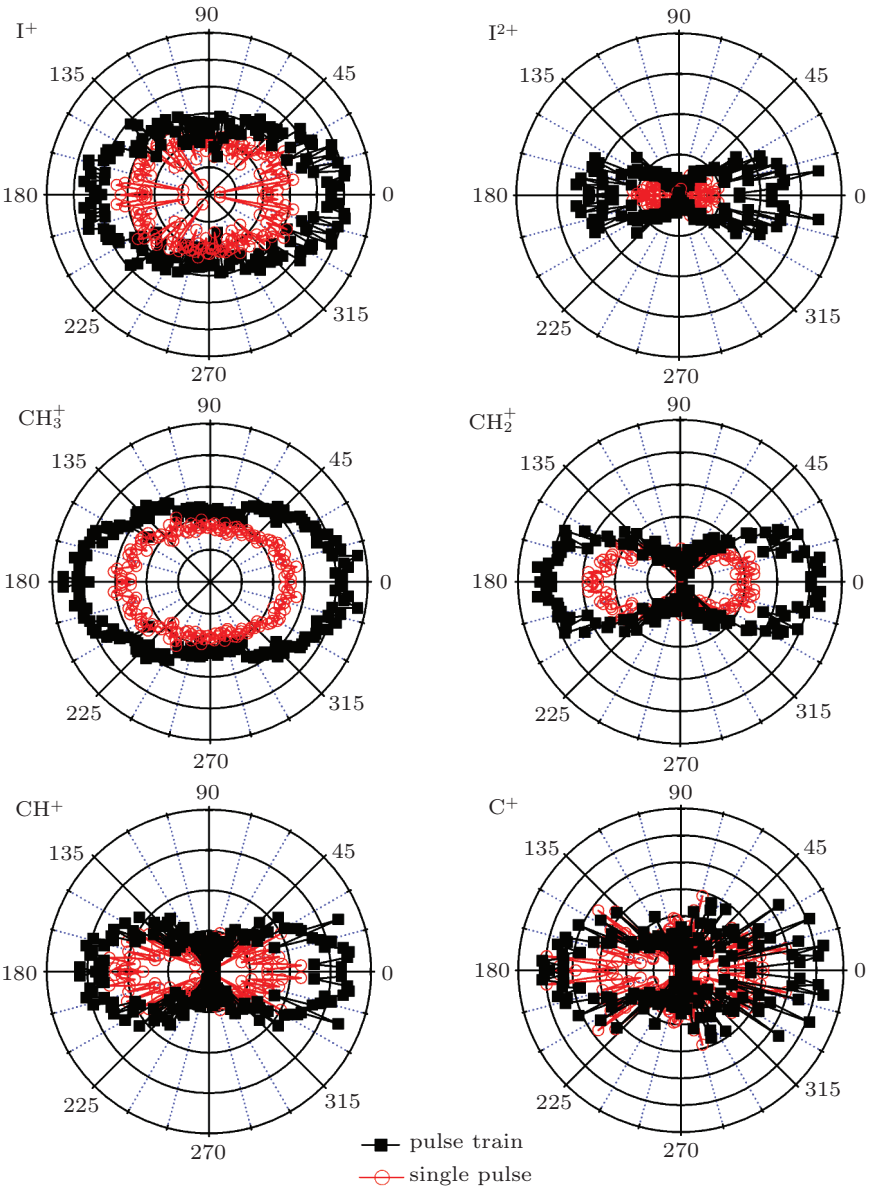



**Fig. 4.** (color online) Angular distributions of $I^+$, $I^{2+}$, $CH_b^+$ ($b = 1$–3), and $C^+$ with a single pulse (red circle) and a train of laser pulses (black square) at the laser intensity of $2.8\times10^{13}$ W/cm$^2$.

In order to characterize the sharpness of the angular distribution, the data are fitted to function $A + B\cos^n(\theta)$, where $A$ is the isotropic component, $B$ is the anisotropic component, and $n$ is the degree of alignment.[30,31] The value of $n$ becomes larger with the increase of molecular alignment degree. The values of $n$ for $I^{a+}$ ($a = 1$, 2), $CH_b^+$ ($b = 1$, 2, 3), and $C^+$ are shown in Fig. 5 for both the pulse train with 200 fs subpulse separation and the single pulse. The alignment degree under the action of the pulse train is not higher than that under the action of a single pulse. It is consistent with the experi-

mental result obtained using a shaped laser pulse for aligning room temperature CO,[32] in which the alignment degree with a pulse shape obtained using a genetic algorithm is not significantly better than that with transform-limited pulses. But it is necessary to analyze why some pulse trains perform at least as well as transform-limited pulses, but others do not. This can be seen in Fig. 3 which shows that the ion intensities of perpendicular polarizations differ mostly at the pulse separation of 200 fs for both $CH_3^+$ and $I^+$, and also in Fig. 5 which shows that the alignment degrees with 200 fs separation pulse train and the single pulse are almost identical.

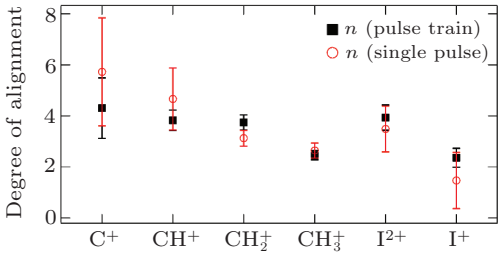



**Fig. 5.** (color online) Degrees of alignment of different fragments with a single pulse and a train of laser pulses.

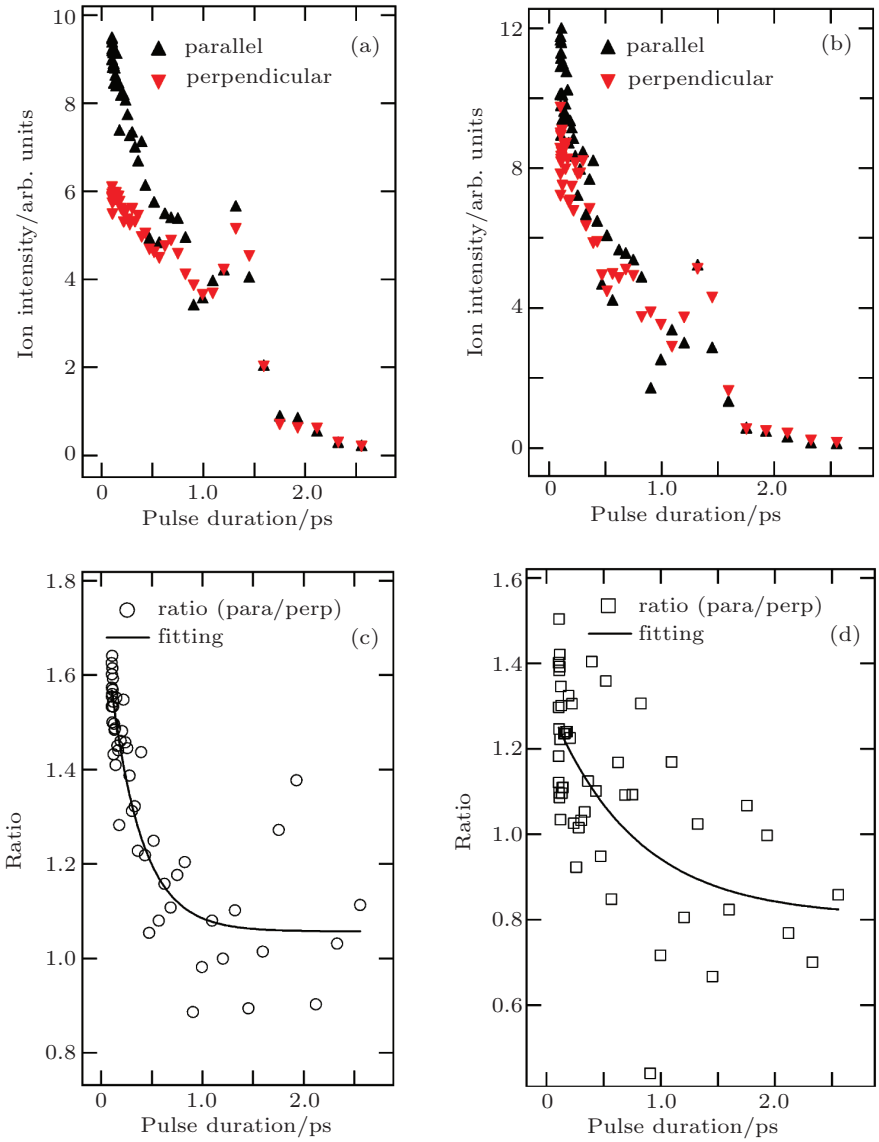



**Fig. 6.** (color online) (a) $CH_3^+$ and (b) $I^+$ intensities at parallel and perpendicular polarizations, ratios of (c) $CH_3^+$ and (d) $I^+$ intensities at parallel to perpendicular polarizations versus the chirped pulse duration.

We try to explain the mechanism of optimizing the alignment in terms of the pulse shape. There are two possible mechanisms. In the first one, the effective duration of the pulse rather than its structure is crucial to nonadiabatic molecular alignment as proposed by Suzuki *et al.*[33] They pointed out that a doubly-peaked pulse with an appropriate interval can be regarded as a single pulse with a center trough based on the considerations from both time and frequency domains. The second possibility is that a dramatic field-free molecular alignment can be achieved after the molecules have been excited with proper trains of strong ultrashort laser pulses as proposed by Leibscher *et al.*[15] They defined optimal two- and three-

pulse excitation schemes. That is, the first pulse is to align the molecules, while the second delayed pulse, which arrives at the time of minimal angular spread of molecules, is to create fragment ions.[34]

In order to verify which mechanism plays a role in our experiment, we investigate the effect of chirping a femtosecond laser pulse on the alignment degree of $CH_3I$. If the pulse duration plays a role, when the effective duration is used, the alignment degree will be enhanced. The effective duration of pulse train equals the sum of the pulse separation in the train and the pulse width.[33] Because the interval between the first and the last pulses is 400 fs and each peak has a pulse width of 90 fs, the effective duration of the pulse train used in our experiment is 490 fs. Figure 6 shows $CH_3^+$ and $I^+$ fragment ion yields obtained at parallel and perpendicular polarizations and their ratios with chirped femtoscond pulses. The ion yields each reach a peak at about 1.3 ps, and the mechanism will be studied in future experiments. Except for the fluctuation at duration values larger than 1.5 ps due to noise from small ion intensities, the ratio reduces as the pulse duration increases and no sign of enhanced alignment is observed for larger duration values. So it is the structure of the pulse train rather than the effective duration of the pulse that is crucial to the nonadiabatic molecular alignment of $CH_3I$ in our experiment.

In future experiments, a pump–probe scheme will be used, in which the pump pulse will be shaped and optimized by a genetic algorithm and its polarization can be rotated. A transform limited pulse will be used as a probe pulse to detect the alignment induced by the pump pulse through processes like Coulomb explosion, alignment dependent ionization, etc. Detection methods like time-of-flight mass spectrum or velocity ion imaging will be used.

## 4. Conclusion

The angular distributions of products of $CH_3I$ under the irradiation of a 90 fs 800 nm linearly polarized laser at a moderate intensity of $2.8\times10^{13}$ W/cm$^2$ are experimentally studied. With a transform-limited pulse, the dynamic alignment dominates according to the dependence of ratio of the ion yields between parallel and perpendicular polarizations of laser intensity. With a three-pulse train of 200 fs sub-pulse separation, the molecular alignment is optimized compared with the other sub-pulse separation pulse trains. It is proposed that the front pulse aligns the molecules, while the later pulse, which arrives at a proper time when the molecules are aligned, creates the fragment ions.

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