Supporting Information

Comment on ‘Closing the Loop on Bond Selective Chemistry Using Tailored Strong Field Laser Pulses’

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1. Pulse characterization

Our experiments were carried out using a regenerative amplified Ti:Sapphire laser (Spitfire-Spectra Physics) seeded by a broad-band Ti:Sapphire oscillator (KM Labs, 45 nm FWHM). The output was centered at 800nm with a repetition rate of 1 kHz and maximum pulse energy of ~800 μJ. The bandwidth was ~28nm FWHM, which results in ~35fs (FWHM) transform-limited (TL) pulses. Phase distortions, second and higher order, from the laser and any optics in the setup were eliminated using multiphoton intrapulse interference phase scan (MIIPS)[1] before any experiment. The characterization of the TL pulses is illustrated in Figure S1 including the fundamental spectrum, normalized second harmonic spectrum (theoretical simulation and experimental data), interferometric and non-interferometric autocorrelations.

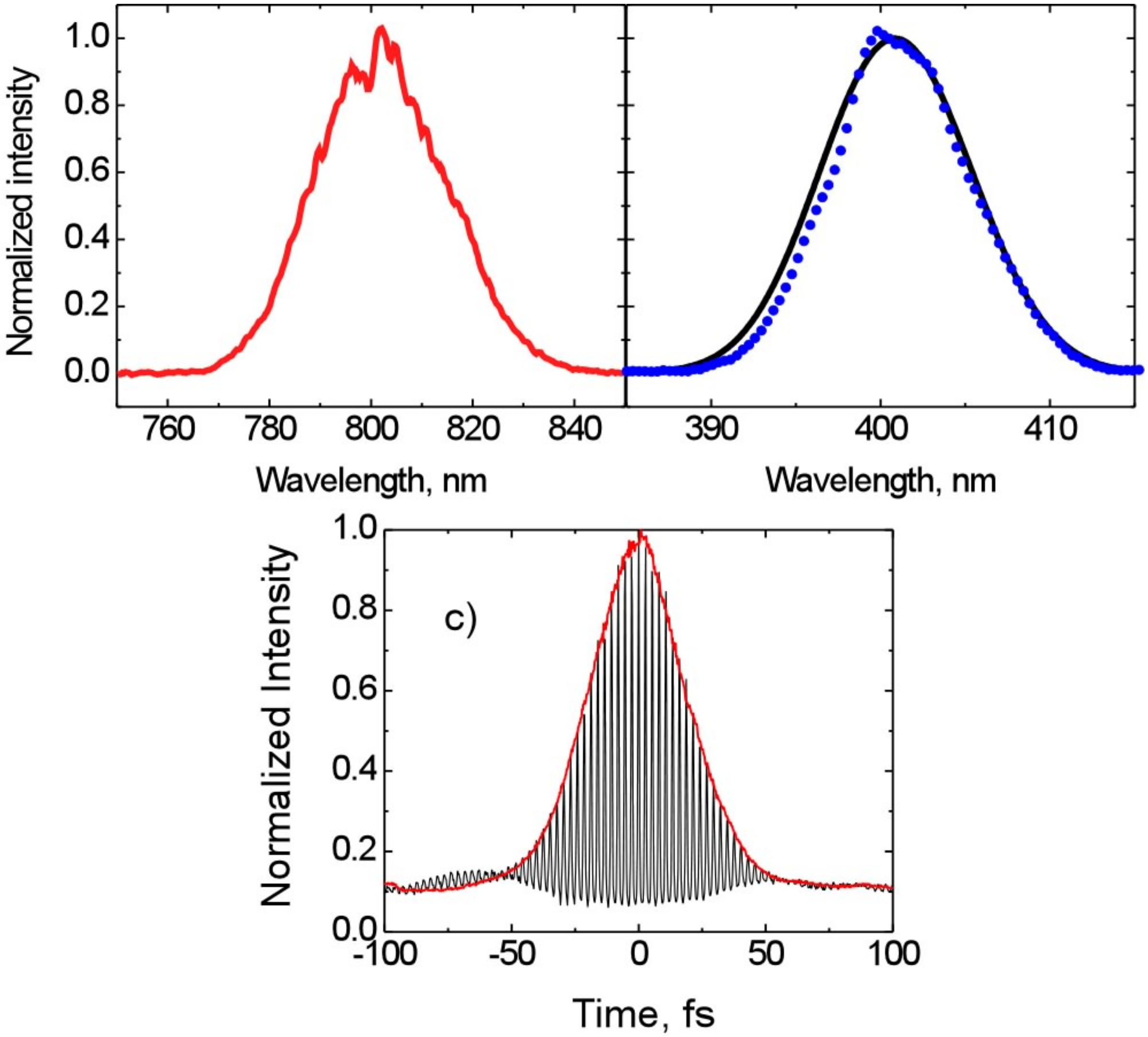


Figure S1. a) Fundamental spectrum of the amplifier output. b) Second harmonic spectrum (SHG) for transform limited pulses (dots), which agrees with the theoretically predicted spectrum (line). c) Interferometric autocorrelation of pulses (black line) and non-interferometric autocorrelation of the pulses (red line). The time duration measured at FWHM is 35.7 fs.

2. Focusing

Two different focusing conditions were implemented for our measurements to achieve a long Rayleigh length (300 mm focal length) and a short Rayleigh length (50mm focal length). The intensity at the focus that can be achieved varies from 10^{12} W/cm^2 to 10^{16} W/cm^2. The spatial profile of the beam was measured using a beam profiler (Coherent) for both conditions. Beam propagation ratio, spot size at the focus and Rayleigh range are summarized in Table S1. The spot size dependences along the optical axis for both focusing lenses are shown in Figure S2; together with the theoretical prediction for Gaussian beams (line). The peak intensities I_0 were calculated for TL pulses using the formula $I_0 = 4\left(\ln\left(2\right)\right)^{0.5}\pi^{-1.5}\times W\times\tau^{-1}\times\omega_0^{-2}$, where W is energy of the pulse (J), τ is the duration (s, FWHM) of the pulse, and ω_0 is spot size (cm, radius where the intensity decreases by e^2 times). The calculated dependence of the maximum field intensity along the optical axis is shown in Figure S2 together with a simulation (Lorentzian line shape).

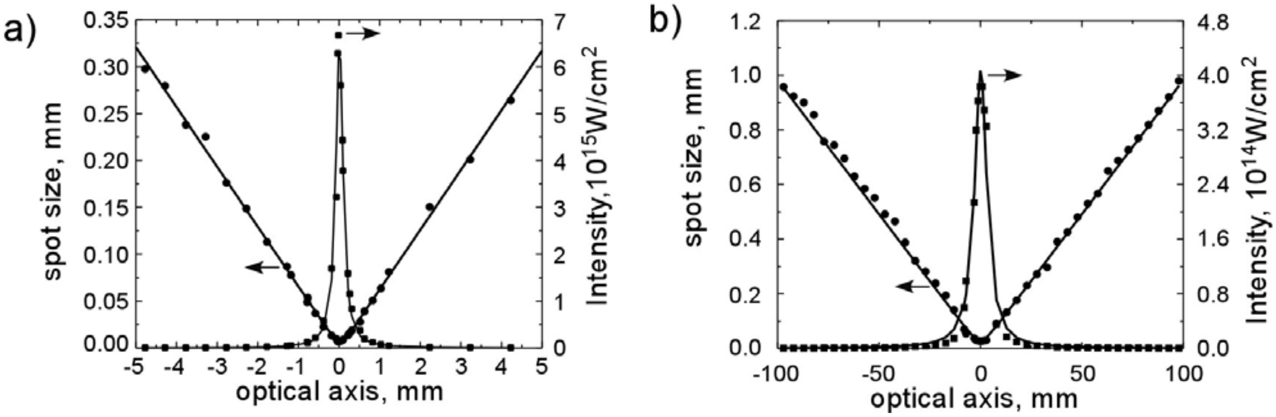


Figure S2. a) Graph showing the measured spot sizes of the beam waist along the optical axis of the laser for the 50mm focal length lens with a Rayleigh length of 66 μm, together with the calculated peak power for 170 μJ TL pulses. B) Graph showing the same as that in b) but for the 300 mm focal length lens with a Rayleigh length of 2.2 mm.

Table S1

Focal length	Beam propagation ratio (M^2)	Spot size at the focus	Rayleigh range
50mm	1.5	6.4 μm	66 μm
300mm	1.04	25.9 μm	2.2 mm

3. Pulse shaping

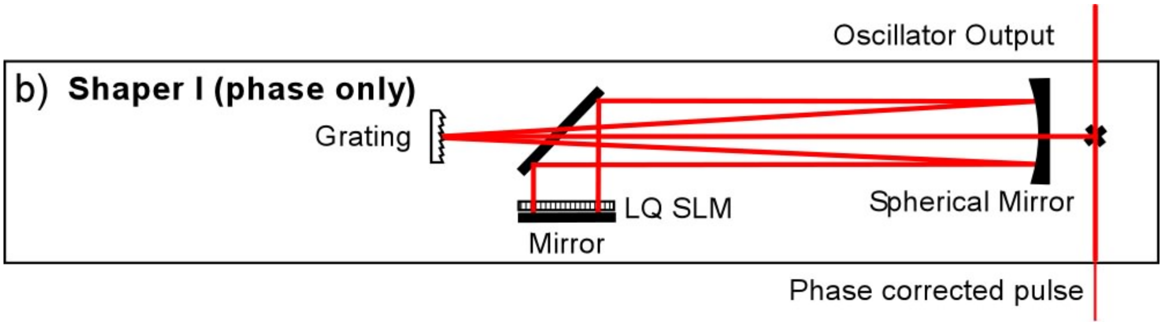
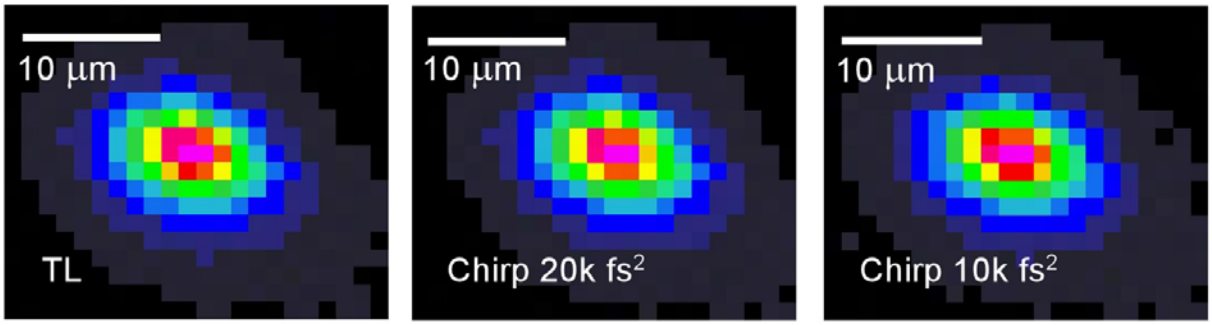


Figure S3. Schematic of a folded phase-only pulse shaper

The pulse shaper (shown in Figure S3) used in our experiment includes an 830 groves/mm dispersive grating, a 15 cm focal length spherical mirror, and a 128 pixel liquid crystal spatial light modulator (SLM-128, CRI) in a reflective mode. In our setup, the pulse shaper is placed before the amplifier. The spectral phase modulation applied by this pulse shaper is preserved during amplification, this has been experimentally verified.[2] As discussed in ref 3, this arrangement reduces the space-time coupling, because the amplifier modes themselves are usually much smaller than the seed laser mode and therefore acts as a spatial filter. Moreover, the optical resolution of the shaper at the SLM is ~30 μm, which is much smaller than the pixel size (100 μm). This prevents space-time coupling distortions. Figure S4 shows the beam profiles obtained at the focus of 50mm and 300mm focal length lenses for pulses with different spectral phases. No space-time coupling distortions are observed.

a) 50mm lens



b) 300mm lens

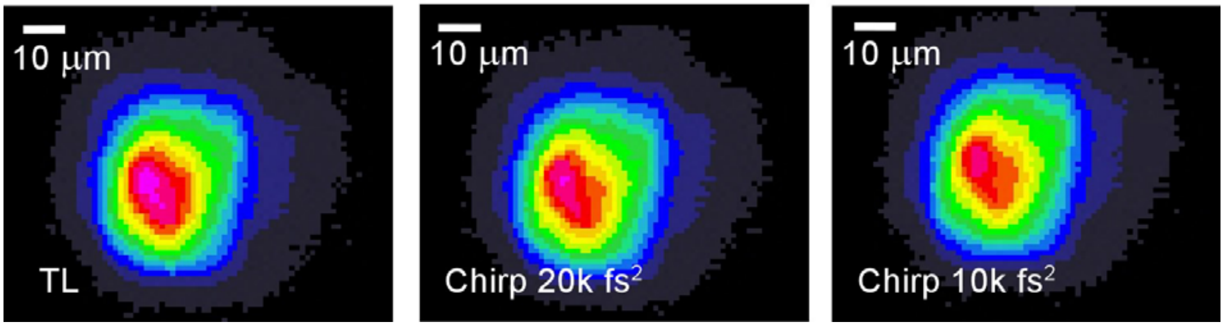


Figure S4. Beam profiles for pulses with TL phase, 20,000 fs^2 positive chirp, 10,000 fs^2 positive chirp at the focus of either 50 mm or 300 mm focusing lens. No evidence for space-time coupling distortions is observed in any of the cases.

To further test our pulse shaper, the integrated intensity of the SHG signal for a chirp scan from -20,000 fs^2 to +20,000 fs^2 was recorded and compared to a theoretical simulation, shown in Figure S5. The agreement between experimental data and theoretical simulation confirms our ability to deliver pulses with desired phases, including transform limited pulses, to the target accurately.

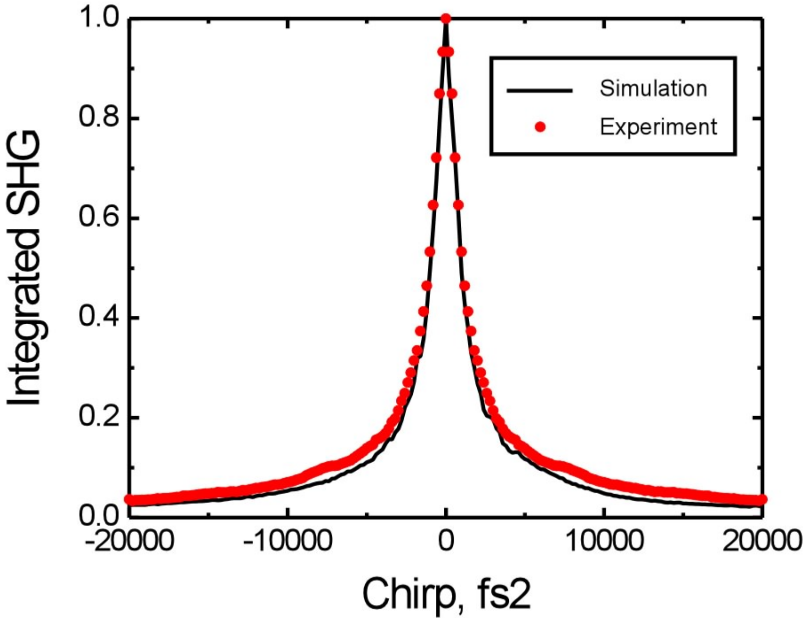


Figure S5. Integrated SHG intensity for a chirp scan from -20,000 fs^2 to +20,000 fs^2 starting with 35 fs TL pulses. Red dots are experimental data and the solid line is the theoretical simulation.

4. Mass spectrometer

Our mass spectrometer has a linear geometry with a 0.5 meter field-free drift region. A base pressure of 10^{-7} Torr was maintained by a three-stage differential pumping system including a mechanical roughing pump, a diffusion pump, and a turbo pump. The sample is introduced into the chamber by a leak valve. In order to prevent the accumulation of photoproducts in the chamber, a pressure of 10^{-5} Torr is maintained when running the experiments by equilibrating the vapor of the sample and the fast pumping speed of the 4 in. turbo molecular vacuum pump. The fast flow is confirmed by observing the fast decay of the signal when closing the valve (See Figure S6).

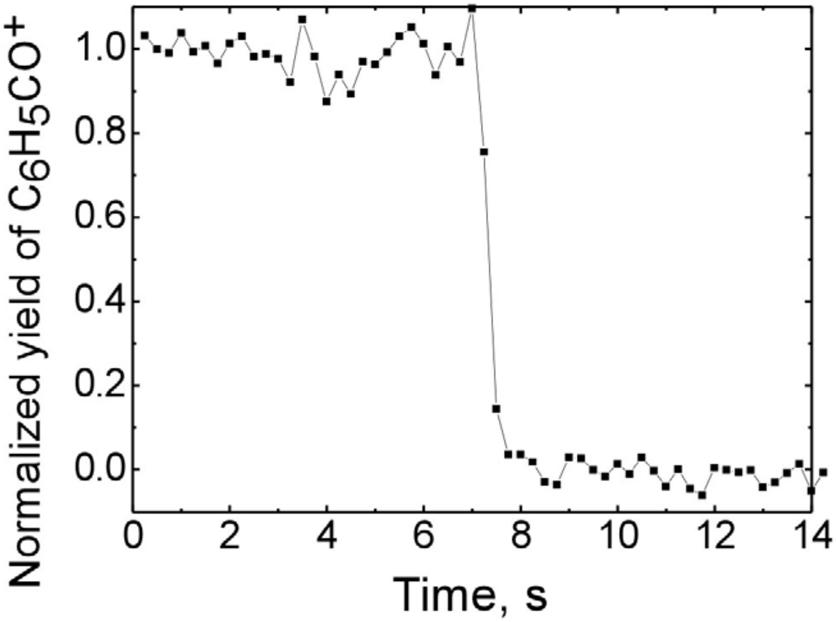


Figure S6. The intensity of $C_6H_5CO^+$, the most abundant photoproduct from acetophenone, drops to zero within a half second after closing the valve, which confirms the fast flow of our system.

In order to reproduce the experimental setup used by Levis' group as close as possible, we collected data for acetophenone using an extraction plate with a 0.66±0.04 mm aperture. Figure S7 shows the mass spectra obtained when 60fs pulses are focused by a 300 mm focal length lens (Raleigh range 2.2 mm) using the aperture. For this experiment, the peak intensity for TL pulses was 1×10^{15} W/cm^2. Assignment of the mass spectra was carried out after careful calibration using eight peaks in order to get accurate *m/z* values. The error is estimated to be in the order of 0.1 *m/z*. No toluene was observed. Note that the relative peak intensities are not in agreement with the spectrum published in Spectrochemica Acta or the one published in 2004 where 60fs pulses were indicated, however the peak assignment in the latter publication is correct and m/z 92 (the toluene ion) was not observed.[4]

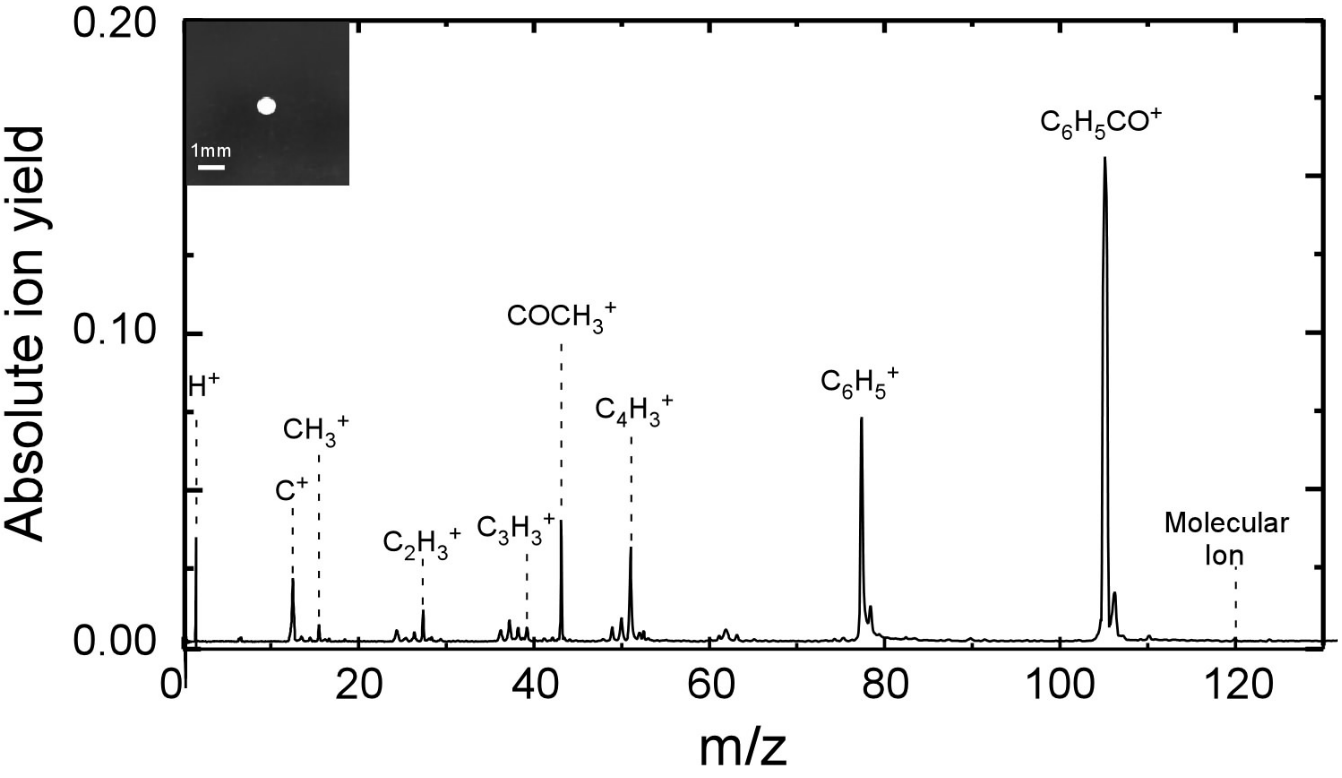


Figure S7. Mass spectrum of acetophenone using 60fs transform limited pulses with a peak intensity at the focus of $1\text{x}10^{15}$ W/cm^2. The inset on the left upper corner is a picture of the extraction plate with a 0.66±0.04 mm aperture located above the focal region where the ions are generated.

According to information provided by Levis (private communication), toluene was observed when the focal spot was 1 cm beyond the aperture. Therefore in our experiment, the focal spot was moved along the beam propagation axis by moving the lens in order to explore the situations when ions formed before or after the focal spot were detected; no toluene ions were observed and no significant change other than the overall intensity of the MS spectra was observed.

It has been argued that the lack of an aperture could give rise to volume effects that would influence the results. This issue has been discussed in detail for our experiments elsewhere.[5] We found that volume effects have little or no effect on controlling fragmentation selectivity above the saturation intensity for ionization. More importantly, no toluene was formed with or without the extraction aperture.

5. Mass spectrum of toluene

The mass spectrum of toluene is dominated by a strong molecular ion peak which is very stable and exhibits very limited fragmentation. When the excitation pulses are chirped, there is very little change in the fragmentation pattern, as shown in Figure S8. The relative yield of the molecular ion is not very sensitive to pulse shaping. If a small amount of toluene contaminant were present when taking the data for acetophenone, the ratio between the toluene ion and any fragment ion from acetophenone would change significantly upon pulse shaping.

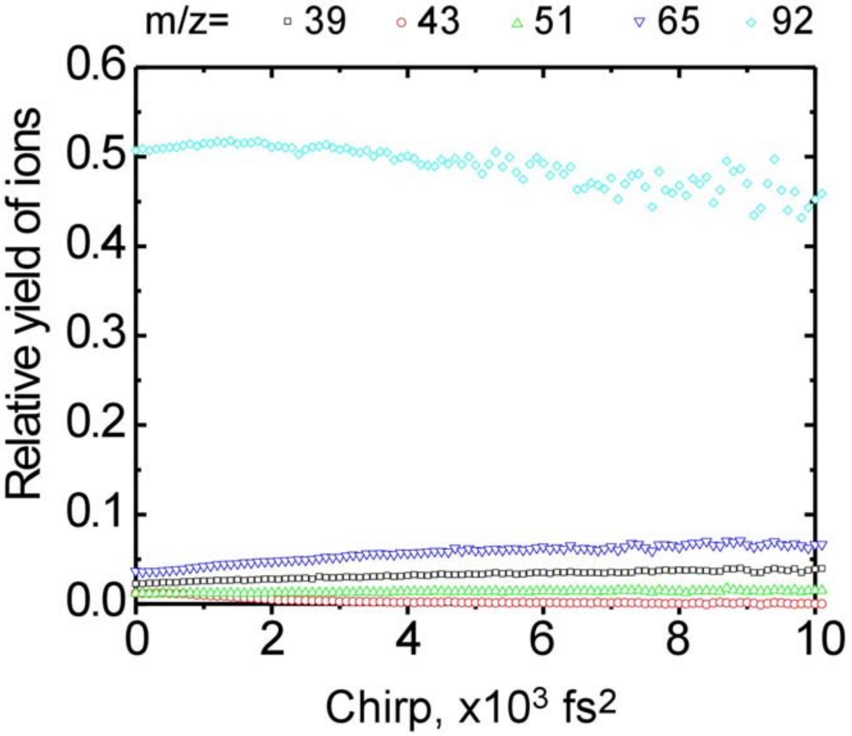


Figure S8. Change in the relative yield of the toluene molecular ion and fragment ions as a function of linear chirp, starting with 35 fs pulses. Note that the H^+ and C^+ ion yields were not taken into account for calculating relative yields.

6. Intensity and time duration

The saturation intensity for ionization of acetophenone is ~1x10^{14} W/cm^2 according to Corkum et al.[6] We examined the fragmentation of acetophenone under intensities below and above the saturation intensity. One alternative to change the laser intensity is to maintain constant pulse energy while increasing the laser pulse duration as done in ref 7. This can be easily and accurately done with our pulse shaper by carrying out a chirp scan. The calculated peak intensity and time duration of the chirped pulses are shown in Figure S9, starting with 35 fs TL pulses having energy of 150 μJ/pulse. As we can see, the intensity at the focus can easily be varied from 5x10^{15} W/cm^2 to 2x10^{13}W/cm^2 while the pulse duration varies from 35 fs to 1.5 ps. By changing the energy of the pulses, the range of peak intensities accessible can be even larger, from 10^{12} W/cm^2 to 10^{16} W/cm^2. Mass spectra of acetophenone were collected for systematic chirp scans with different pulse energy. Part of the data is shown in Figures S10 and S11. Toluene was not observed under any conditions.

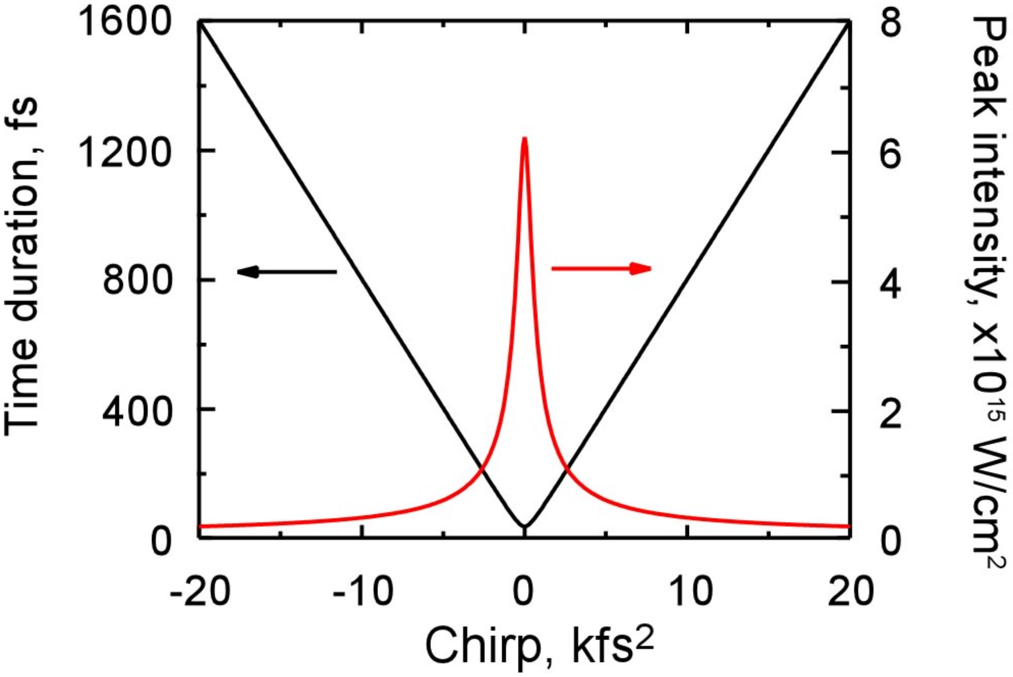


Figure S9. Calculated pulse duration and peak intensities for pulses chirped by up to ±20,000 fs^2, starting from 35 fs TL pulses with pulse energy of 150 μJ.

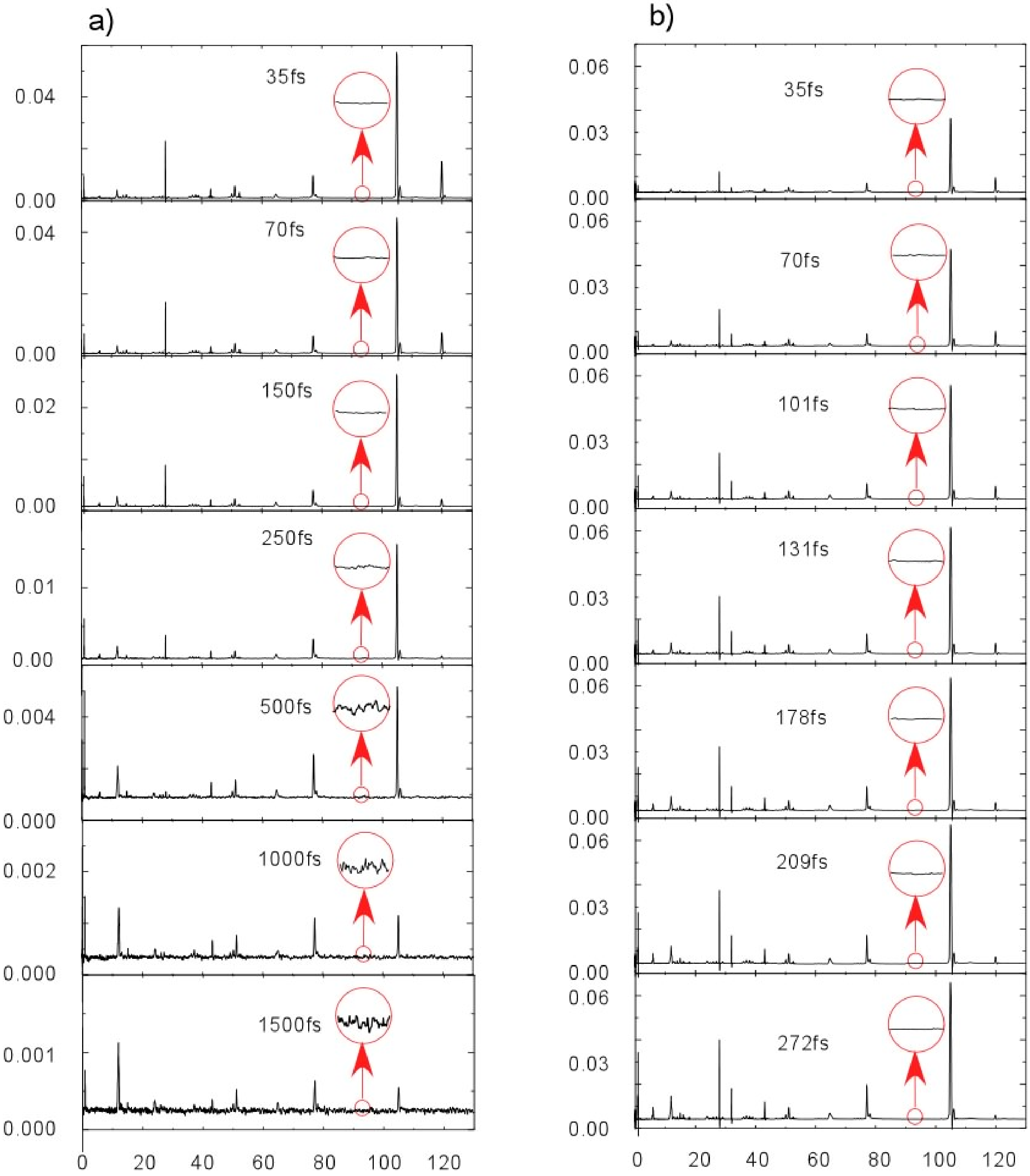


Figure S10. a) Mass spectra of acetophenone obtained as a function of linear chirp. The pulse duration increases from top to bottom; b) Mass spectra of acetophenone obtained from pulses with different time durations but maintaining the same peak intensity 1x10^{15} W/cm^2 at the focus. The insets in all cases are magnifications (x10) of the mass spectra in the range of m/z between 91 and 93, where the toluene ions would be expected if formed.

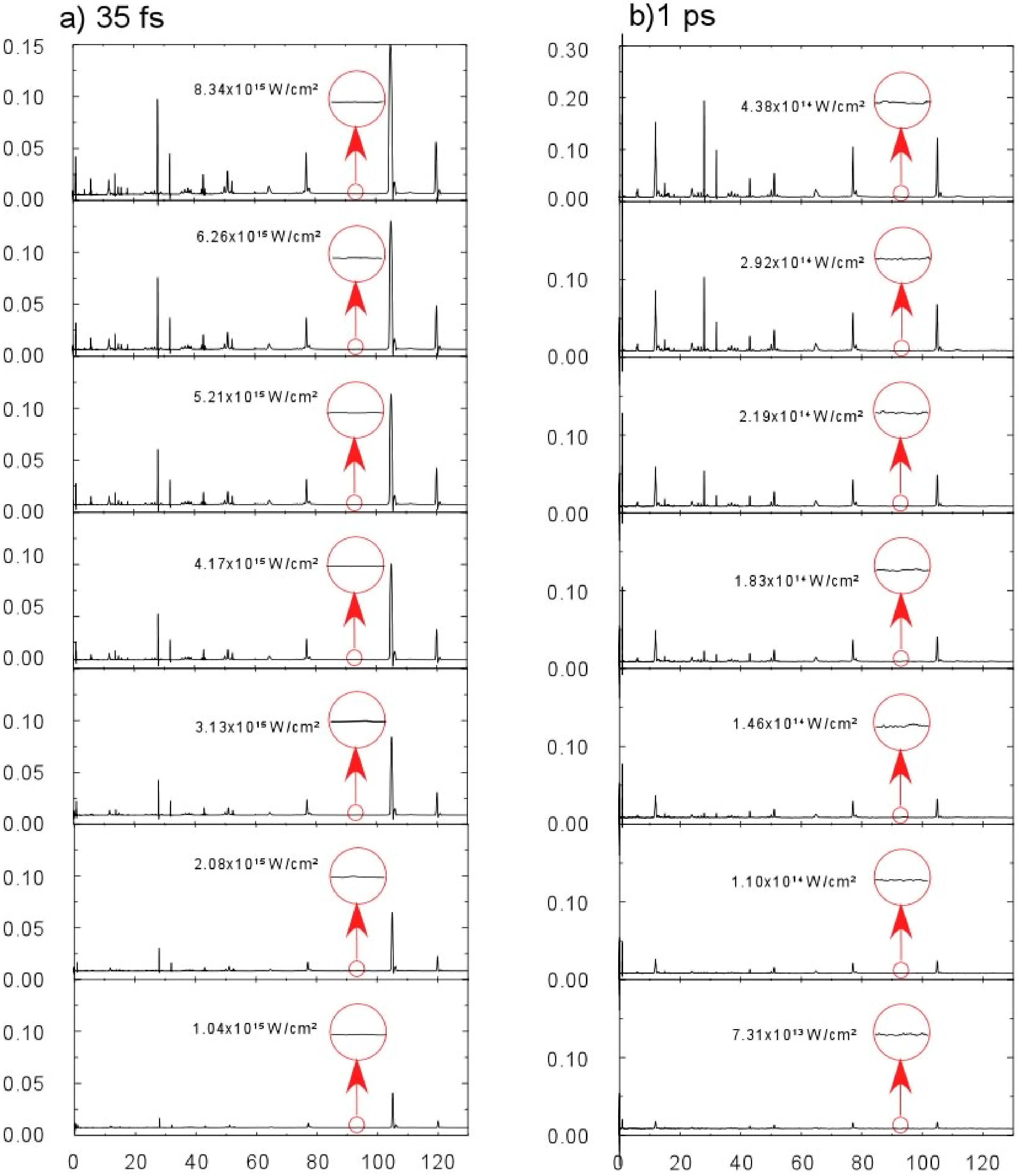


Figure S11. a) Mass spectra of acetophenone obtained for 35fs transform limited pulses at different peak intensities at the focus; b) Same as a) but the pulse duration is changed to 1 ps. The insets in all cases are magnifications (x10) of the mass spectra in the range of m/z between 91 and 93, where the toluene peak would be expected if formed.

In conclusion, we have not been able to reproduce the formation of the toluene cation from acetophenone under Levis' experimental conditions, and no toluene has been observed under any other experimental condition.

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