

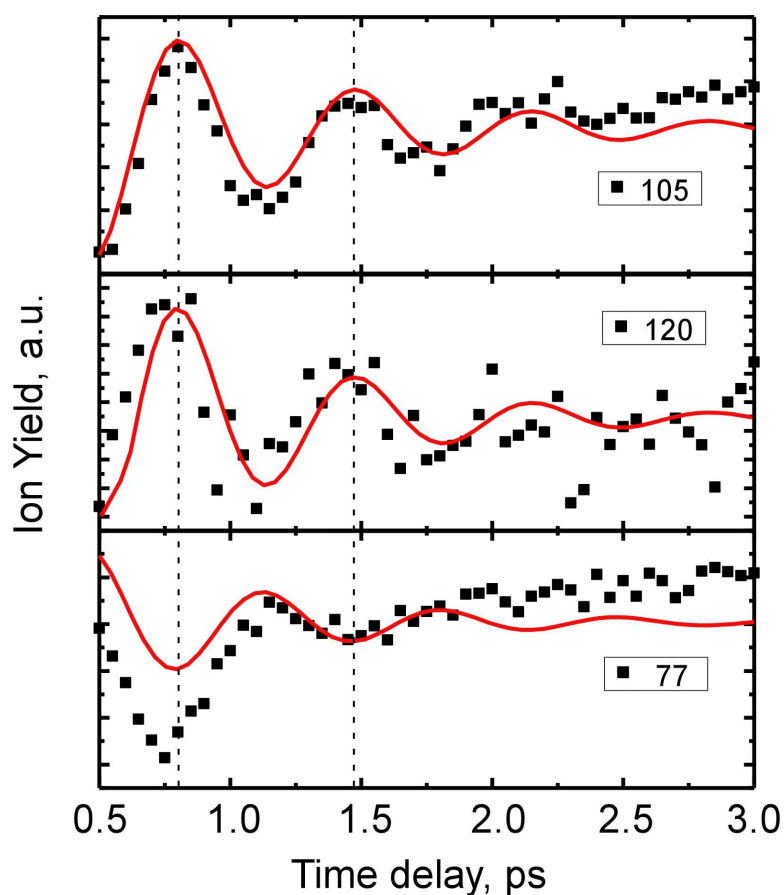
**Supporting Information for “*Photodissociation dynamics of acetophenone and its derivatives with intense non-resonant femtosecond pulses*”**

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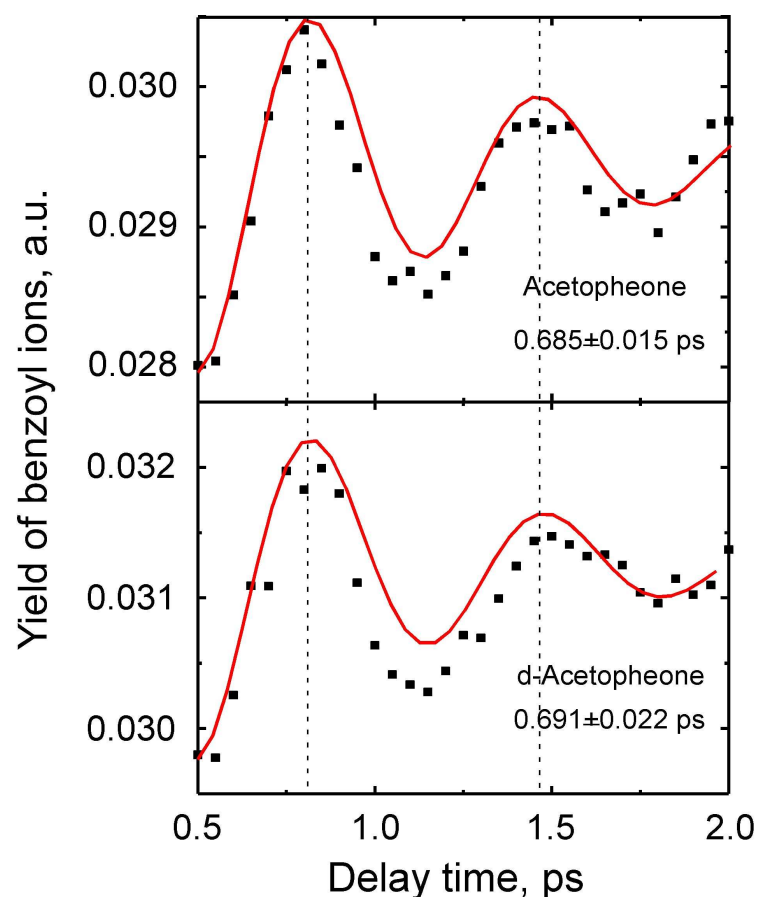
## **1. Data Fitting**

Fittings of the oscillations observed in the yield of benzoyl ions generated from acetophenone and its derivatives are performed with a mathematical model that includes a sine function with an exponentially decaying amplitude  $y = ae^{-\frac{x}{\tau}} \sin(\omega x + \varphi) + c$ , where  $2\pi/\omega$  gives the oscillation period,  $\varphi$  is the phase, and  $\tau$  is the dephasing time. The results are shown in Figs. S1 – S3. The fittings for different ions ( $m/z=77$ , 105, 120) in Fig. S1 show that all the ions oscillate with the same period. We observe that the phenyl ion ( $m/z=77$ ) oscillations are out of phase compared to the benzoyl ion and the molecular ion.



**Figure S1.** The yields of three ions ( $m/z=77$ , 105, 120) generated from acetophenone in pump (TL) probe (Chirp) experiments described in the paper and their fittings.

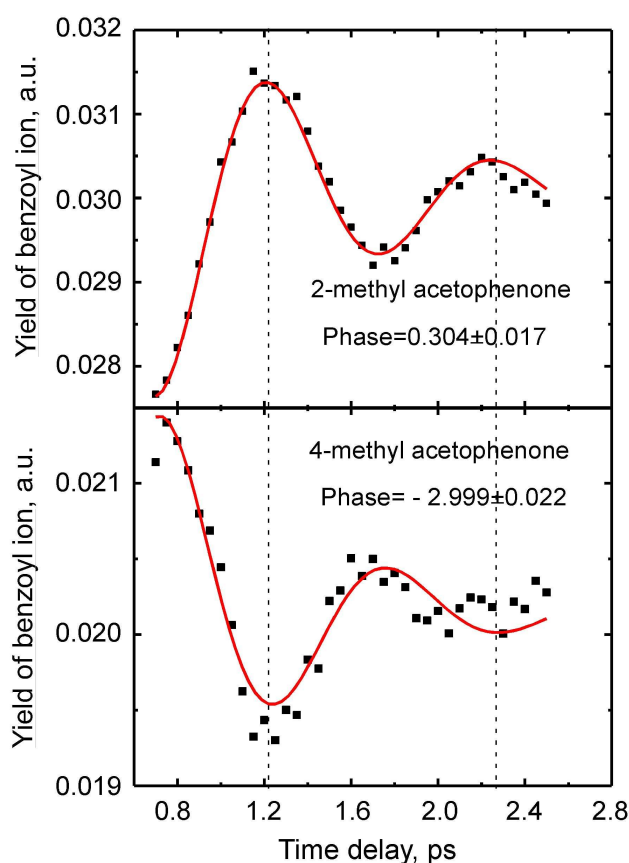
Shown in Fig. S2, The period of oscillation measured for acetophenone ( $0.685 \pm 0.015$  ps) and partially deuterated acetophenone ( $0.691 \pm 0.022$  ps) are reasonably close. Although the difference is within our experimental accuracy, it makes sense that the slightly heavier partially deuterated acetophenone would have a slightly longer period.



**Figure S2.** The yields of benzoyl ions generated from acetophenone (top) and d-acetophenone (bottom) in pump (TL) probe (Chirp) experiments described in the paper and their fittings.

The data for 2-methyl acetophenone and 4-methyl acetophenone are shown in Fig. S3, the periods measured for these are  $1.033 \pm 0.034$  ps and  $1.040 \pm 0.030$  ps respectively. Interestingly, this period is ~50% longer than that measured for acetophenone and partially deuterated acetophenone. The main difference arises from the methyl in the aromatic ring. Methyl is considered to be electron donating, compared to hydrogen. The longer period found for the 2-methyl and 4-methyl acetophenones indicates that the torsional force constant is weakened by this substitution. In addition, it is interesting that the relative phase

difference between the oscillations from both methyl substituted compounds is found to be  $(1.051 \pm 0.013)\pi$  implying that the oscillations from these two molecules are exactly out of phase. We do not know the reason behind this observation and plan to explore this further.

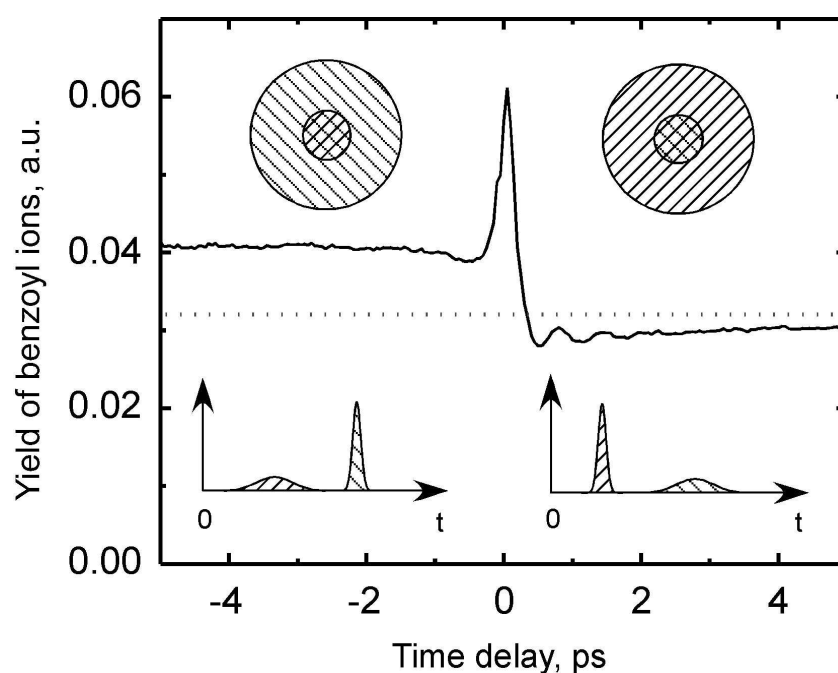


**Figure S3.** The yields of benzoyl ions generated from 2-methyl acetophenone (top) and 4-methyl acetophenone (bottom) in pump (TL) probe (Chirp) experiments described in the paper and their fittings.

## 2. Rationale for using a TL pump and a chirped probe pulse

After observing the oscillations in the ion yields following TL-TL experiments, we wanted to get data with better signal to noise ratio. We knew that we didn't need very short pulses, we also wanted to make sure that the signal measured was primarily arising from molecules that had already been ionized by the pump pulse. This would require us to attenuate the probe pulse, however attenuation would

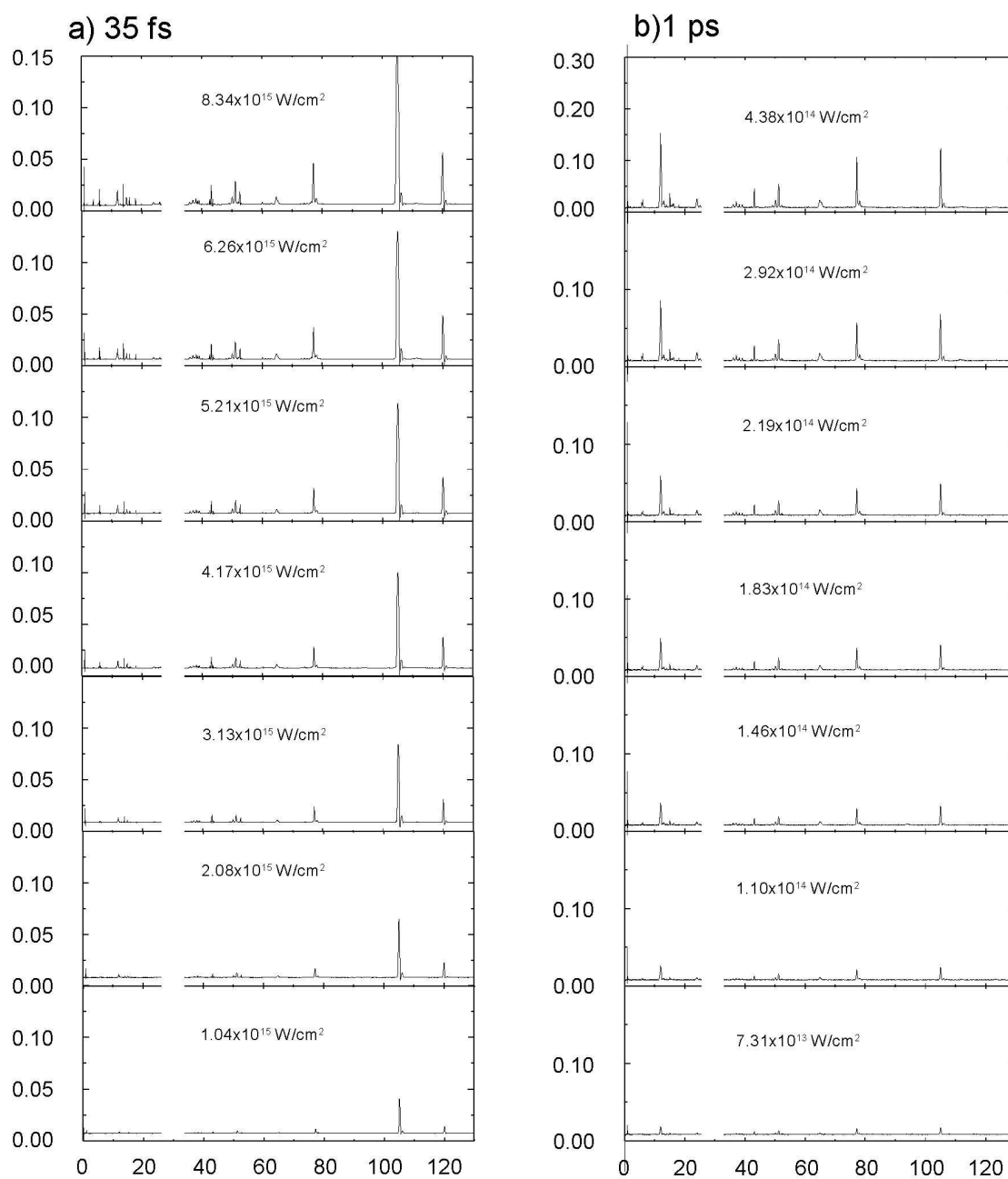
lead to lower signal level and lower signal to noise ratio. Therefore, we decided to reduce the peak intensity of the probe by introducing sufficient chirp that the ionization caused by the probe alone was negligible. We know this setup was successful by analyzing data such as the one shown in Figure S4. We see that for positive times, the amount of ionization caused by the pump laser (dashed line) is maximized. The probe laser only reduces the number of benzoyl ions by causing further fragmentation. Analyzing the data obtained for negative time delays, it is clear that more benzoyl ions are observed than those formed by the single TL pulse. In this case the probe interacts first with ground state molecules and creates some excitation and a small amount of ionization, then the TL pulse causes additional ionization but none of the dynamics of interest. For positive times the TL pulses ionize a greater sample volume than the lower peak intensity probe laser. Therefore, at positive times the probe laser only probes molecules that had been ionized by the TL pulses, as desired.



**Figure S4.** The yield of benzoyl ions for time delays from -5ps to +5ps generated from acetophenone using one TL pulse and one chirped pulse. The circles indicate the area at the focus where the laser intensity is above the ionization threshold. The order of pump and probe lasers is indicated below, the hatch direction helps identify the respective volume sampled by pump and probe lasers.

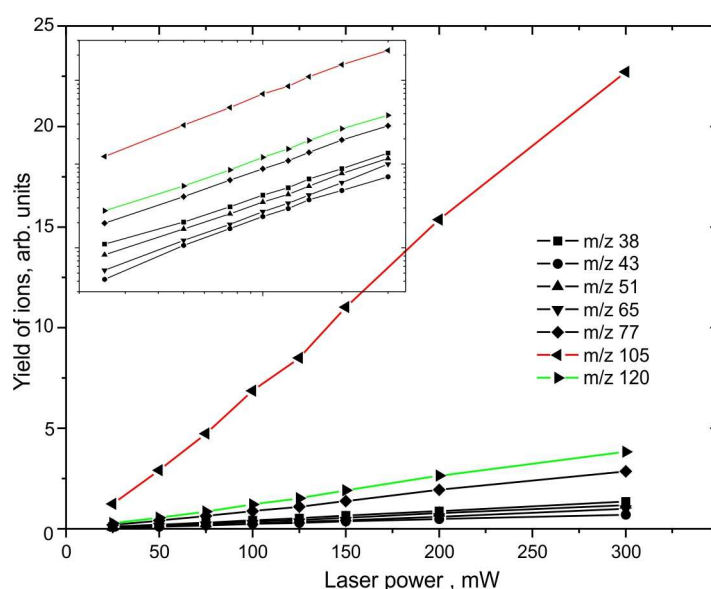
### 3. Volume effect

Given that laser induced ionization is the only source of signal in the experiments presented in this article, it is important to determine if different products are observed as a function of different laser peak intensities. This is because the Gaussian distribution of laser intensity of the focusing beam would produce a distribution of fragments if the products were peak intensity dependent. Furthermore, any change in the laser peak intensity caused by chirp, for example, would also lead to the production of different fragment ions. This laser intensity dependence is sometimes referred to in the literature as the *volume effect*.<sup>1</sup> When carrying out experiments using a pulse shaper, it is important to rule out the dependence of the observed fragmentation on the lasers peak intensity. The results shown in Fig. S5 demonstrate that the resulting fragment ions for acetophenone are independent of peak intensity. The first column shows the time-of-flight spectra obtained with 35fs TL pulses with different power.



**Figure S5.** Time of Flight mass spectra for time delays from -5ps to +5ps generated from acetophenone using one TL pulse and one chirped pulse. The region for  $m/z$  from 27-33 are blocked due to the signal from oxygen and nitrogen molecules from air.

The data in Figure S5 was analyzed by integrating each  $m/z$  region. This was important because some of the strongest peaks showed some space-charge broadening, making their intensity not proportional to their integral. Figure S6 shows the intensity dependence on the yield for the major fragment ions produced from acetophenone. Figure S6 (inset) is a double logarithmic graph of the yield of ions versus the laser power. In both cases, the yields depend linearly with power dependence, suggesting that the volume effect is primarily to increase the signal intensity but is not responsible for observing different fragmentation pathways.



**Figure S6:** Ion yields of main fragment ions generated from acetophenone are plotted against varying laser power. (Inset): The logarithmic plot of the yield of main fragment ions against varying laser power. Yield of ions were measured experimentally by integration of TOF mass spectrum peaks.

In this study we looked at the time-dependent processes occurring after intense non-resonant excitation. The signal when pump and probe pulses are not overlapped in time (after the first 40fs, or 200fs when we used a chirped probe)



the laser intensity stays constant. Therefore, measurements of relative ion yields under these conditions are immune to the intensity variations at the focal volume.

#### References

- 1) Posthumus J. H.; Rep. Prog. Phys. **67** (2004) 623–665