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Reply to “Comment on ’Closing the Loop on Bond Selective Chemistry Using Tailored Strong Field Laser Pulses’”: Experimental Requirements for Strong Field Control in the Picosecond Regime

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In the course of strong field chemical control experiments Zhu et al.[1] found no evidence for the formation of the toluene rearrangement product reported in 2001[2] and included in a feature article in the *The Journal of Physical Chemistry A*.[3] Zhu et al. correctly point out that a subsequent measurement we reported in a conference proceeding contribution using a conventional femtosecond pulse shaping apparatus was misassigned by Graham et al.[4] The misassignment was based on an incorrect plot of the data in the time-of-flight mass spectrum using time space rather than mass space. The correct assignment of mass spectral features is shown in Figure 1 of the comment by Zhu et al. Figures 3−9 in the Graham et al.[4] paper should then be interpreted as the dependence of the m/e^- 51/105 fragment as a function of chirp. We acknowledge Zhu et al. for correcting this mistake. We would also like to note that the CH_3OF product noted in Figure 16 of the *JPC* article[3] is likely assignable to CF_2

Zhu et al. then incorrectly proceed to extrapolate their measurements to claim that the original report[2] of the isomerization/dissociation product is also incorrect. This is based on the Zhu et al. claim to have reproduced the experimental shaping apparatus in the original paper and to have measured no evidence for the isomerization/dissociation product. In fact, they did not reproduce the laser system creating the shaped pulses, nor did they reproduce the pulse shape parameter space used for the experiments. So, it is not surprising that they found no evidence for the reaction. The preponderance of the comment by Zhu et al. seeks to support the hypothesis that shaped laser pulses are incapable of creating the dissociation/isomerization product toluene from acetone, and this hypothesis can not be supported by their limited measurement space.

Zhu et al. have shown, in agreement with the now correctly assigned spectrum from ref 4, that shaped pulses of duration ~60 fs are likely incapable of creating the putative toluene product. The experiments performed in ref 2, however, employed a unique pulse shaping arrangement where the liquid crystal modulator was placed directly into the Fourier plane of a 60 cm reflective stretcher, before the regenerative amplifier. This has two important consequences for the comparison, and we communicated these to the MSU group on several occasions. The pulse duration from the regenerative amplifier *without* the pulse shaper in the stretcher was 60 fs, the pulse duration *with* the pulse shaper in the stretcher was not measured but can be estimated to be approximately 10−50 times longer. As a consequence, the figure captions for Figures 14, 16, and 18 in ref 3 should be changed from 60 fs to ~1 ps. Our shaper within the stretcher system also produced maximum pulse energies in the picosecond regime that are 10 to >1000 times greater than that available from the MSU system depending on the pulse duration in question. We conclude that different intensity and pulse duration spaces are probed in these two experiments. Without the longer duration pulses and the higher energy pulses, one anticipates little strong field excitation for the MSU system in the picosecond regime.

Under the conditions described, we measured a signal at m/e^- = 92 when the laser pulse interacted with acetophenone, and we assigned this feature to toluene. As reported in ref 2, we also detected a peak at $m/e^- = 95$ from similar experiments on deuterated-acetophenone ($C_6H_5COCD_3$), corresponding to the expected deuterated-toluene product. The electron impact mass spectra taken of the samples displayed no toluene impurity in either the acetophenone or the deuterated-acetophenone samples employed. Note that without some detectable signal to start with, it is not surprising the Dantus experiment could not use the power of optimal control to determine a viable photonic reagent for isomerization/dissociation. The lack of toluene signal may be attributed to the difference in excitation parameters as described next. The fact that mass spectral product distributions are quite sensitive to laser conditions is highlighted even in the Zhu et. al measurements. For instance, in Figure 1 of Zhu et. al. there is no feature at m/e 89, this spectrum presumably results from tight focusing as evidenced by the cracking pattern (the ration of m/e^- 105/1 ~ 1) and high mass spectral resolution. Note that in Figure 2 of Zhu, there is a distinct peak at m/e 89, which is 3 amu from the m/e 92 in question in this Comment. Figure 2 presumably results from much looser focusing, as evidenced by the lower mass spectral resolution and much reduced mass spectral fragmentation (ratio of m/e^- 105/1 ~ 16).

Concerning the comparison of one laboratory’s data to another laboratory’s data using shaped, strong field pulses, it is well-known in the ultraintense laser community that unique spatiotemporal profiles can be created with small changes in pulse shaper design and focusing geometries.[5−7] Furthermore, the binary phase shaper design employed in the Zhu et al. measurements can have serious spatio-temporal coupling limitations, particularly if the shaper is located after the regenerative amplifier, as there will always be some frequencies spanning pixel pairs.[8] In comparing the Zhu et al. design to our original design, there are very significant differences and thus it does not surprise us that different chemistries are observed between the two systems. Some of the data shown in the Zhu et al. comment, specifically Figure 1 and 3, are acquired using tight focusing (*f*/5) conditions as described in ref 1 of Zhu et al.[9] This results in a 30 μm Rayleigh length and 5 μm diameter while that in our paper[2] uses *f*/100 optics with a 3 mm Rayleigh length and 100 μm diameter. In addition to 4 orders of magnitude enhancement in sensitivity in our experiment, we use a 500 μm aperture to eliminate volume averaging that the MSU group surprisingly maintains does not make a difference.[9] The lack of an aperture is known to give rise to obfuscation of signal and uncertainty in interpretation,[10] and the assertion by the MSU group that focusing conditions and apertures make no difference is unique in the strong field community. Comparison of Figure 1 (no $m/e = 89$) and 2 (significant $m/e = 89$) from Zhu et al. demonstrates the significant changes that occur in fragmentation products as a function of focusing conditions.

As for Figure 3, Zhu et al. show that there is substantial chirp control for $m/e^- = 105$. This is completely expected given the

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tight focusing conditions, the lack of an appropriate aperture and the considerable spatio-temporal coupling employed in their binary phase pulse shaping method. In fact, the results presented in Figure 3 of the Comment and all of the measurements presented in ref 1 of Zhu[9] suffer from exceeding the saturation intensity for ionization[11] and volume effects from the lack of an aperture.[5] Any connection to processes occurring below the saturation threshold for ionization are obscured by the experimental conditions the MSU group employs. Thus, one wonders how any comparison can be made between the Graham et al. and Zhu et al. measurements in light of the focusing differences.

To make a meaningful comparison between different laboratories, a method is required to independently measure the complex laser pulses resulting from a laser pulse shaping system. Until very recently,[12,13] this was essentially impossible for complex pulses. It is well-known in the chemistry community that just as there are innumerable ways to perform an experiment such that a desired reaction will *not* work, there are often few productive routes to inducing a complex reaction. To posit our observation of toluene from acetophenone to spiked impurity is counterproductive given the differences in the laser pulses, pulse shapers, and focusing geometries employed.

We learn from the Zhu et al. Comment that while shaped femtosecond pulses appear to be excellent drivers of photodissociation/ionization, such pulses in the *femtosecond* duration regime are likely not optimal for driving molecular rearrangements. In conclusion, another hypothesis may be proposed for the observations: Shaped picosecond laser pulses are necessary to drive rearrangements of complex polyatomic molecules when large scale motion (3−10 Å) is required for the reaction. This notion was discussed previously in our feature article.[3]

References and Notes

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