COMMENTS

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

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Received: May 22, 2007; Revised Manuscript Received: April 30, 2008

Our research on time-of-flight mass spectrometry (TOFMS) coupled with controlled molecular fragmentation and ionization using shaped femtosecond pulses as a means for molecular identification has led us to uncover general trends that describe how molecules behave under intense laser radiation.[1] One of the reviewers of that work suggested that we include in the study a molecule with a known behavior under shaped laser pulse irradiation. Among the many different molecules evaluated, we explored acetophenone which was the subject of the most important laser control experiment.[2−4] The work by Levis and Rabitz in the field of laser control achieved great importance due to their result of having controlled a complex bond rearrangement reaction (Scheme 2, in ref 2; Scheme 3c in ref 3), specifically the production of toluene starting from acetophenone (see Figure 1 insert). Their original experiment was reported to *Science*,[2] a more extensive discussion on bond selective chemistry using tailored strong field laser pulses was published as a feature article in this journal,[3] and finally, an investigation of the effects of experimental parameters was published in *Spectrochimica Acta*.[4] To our surprise, we were not able to reproduce their results.

Their mass spectrum for acetophenone (10^{-5} Torr) taken with 800 nm, 60 fs transform limited pulses at an intensity of $\sim 10^{13}$ W/cm^2 according to their caption shows a prominent peak assigned to *m/z* 92 identified as toluene.[2−4] We attempted to reproduce their experimental conditions as closely as possible (sample pressure at 1.1×10^{-5} Torr, 800 nm, 60 fs transform limited pulses at a peak intensity of $\sim 10^{13}$ W/cm^2). Focusing the 10 mm diameter beam with a 300 mm focal length lens and using an extraction plate with a ~0.5 mm aperture see Figure S7 in Supporting Information where details of the instrumentation and experimental conditions can be found. We used acetophenone (Fluka, purity >99.5%) and performed a conventional GC−MS analysis to confirm the identity and purity. In order to match the relative intensity of peaks *m/z* 77 and 105 to those found in Figure 1 ref 4, we had to use 600 fs pulses (see Figure 1). Every line in our spectrum matches a corresponding line in their spectrum with an accuracy that is better than the line width. The distribution pattern of the fragment ions is quite similar in both cases, indicating we matched the experimental conditions. However, we disagree with their assignment. Their spectrum indicates the abscissa is mass to charge, but we find that it corresponds to time-of-flight.

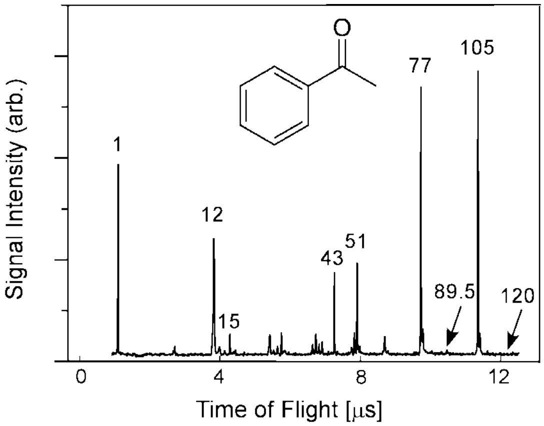

Figure 1. Mass spectrum of acetophenone under intense 800 nm excitation with 600 fs pulse that is comparable with that of Figure 1 in ref 4.

Because mass to charge depends on time-of-flight squared, their spectral assignment was incorrect. The peak assigned to toluene (*m/z* 92) was the expected benzyl radical ion $C_6H_5^+$ (*m/z* 77). We believe all other peaks (except for *m/z* 105) were erroneously assigned. Figure 1 show the correct *m/z* assignments. The excellent agreement at all *m/z* values together with the similar intensity distribution pattern between their data and ours indicates that the experimental conditions were sufficiently similar. We find no evidence for toluene production in this experiment, and suggest their data in ref 4 show no evidence for toluene either.[4]

Next, we attempted to reproduce the data published in their original *Science* paper (Figure 5a in ref 2; Figure 18 in ref 3). The experimental conditions given for their measurements were 60 fs pulses and a peak intensity of 5×10^{13} W/cm^2 (according to Figure 18 caption, in ref 3). Differences between the spectrum shown in refs 2 and 3 with that published in ref 4 indicate the conditions stated cannot be correct. We contacted Levis to make sure that every detail of their experimental setup was reproduced. He indicated pulses may have been as long as 200 fs. We reduced the bandwidth of our laser to 10 nm and increased the duration of the pulses to match as closely as possible the experimental conditions indicated. We were not able to reproduce their results.

In our efforts to reproduce their results we explored a wide range of laser pulse durations and intensities using two different experimental setup. By using a long focal length lens 300 mm or a short focal length lens 50 mm (2.2 and 0.066 mm Rayleigh length, respectively, as shown in Figure S2), we were able to achieve peak intensities in the range 10^{13} to 10^{16} W/cm^2. Experiments were carried out with an extraction mesh, a pinhole, or a slit at the extractor plate; see ref 1 for a full description of our setup. We also explored changing the location of the laser focus with respect to the position of the extraction pinhole, following a suggestion by Levis that toluene was observed when the focus of the laser was 1 cm beyond the extraction pinhole (email communication). We explored longer pulses (up to 1 ps) and shorter pulses (35 fs); we also explored a number of different pulse shaping strategies. None of these experimental

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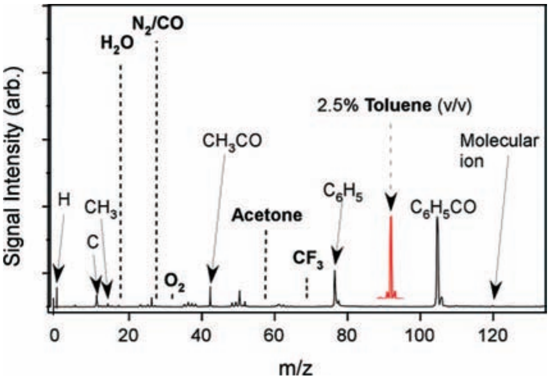

Figure 2. Mass spectrum of acetophenone under intense 800 nm excitation with 200 fs pulses. The arrows point to peak assignments. The dashed lines indicate ions and relative abundance (approximate peak height) observed in Figure 5A[2,3] or Figure 18[3] but not observed in our data. When 2.5% (v/v) of toluene was added to our acetophenone sample, the spectrum remains identical except for the appearance of the toluene ion peak with *m/z* 92; see red inset.

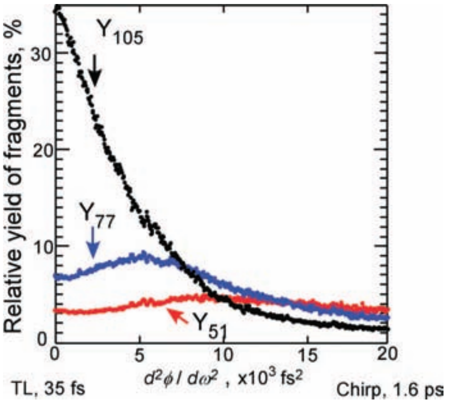

Figure 3. Dependence of relative ion yield for selected ions resulting from acetophenone excitation as a function of positive linear chirp. Note the significant changed observed in the relative yields as a function of chirp compared to almost no changes observed in Figure 8 from ref 4.

variables resulted in the observation of *m/z* 92 ions (see Figures S10 and S11). This is in contrast with their finding of toluene ions being a major peak for 60 fs transform limited pulses.

The acetophenone mass spectrum published in Figure 5A,[2] and in Figure 18,[3] obtained with transform-limited pulses, was then compared to our experimental spectrum, obtained under similar (long focal length and extraction pinhole) conditions, shown in Figure 2. The C_6H_5CO and C_6H_5 ions, as well as some minor unassigned (H, C, CH_3, CH_3CO) ions, are in agreement with our findings. Closer analysis of their spectrum suggests that there were several contaminants in their mass spectrometer chamber including strong peaks for H_2O, N_2/CO, O_2, acetone and CF_3 ions. Evidence for this observation comes from the results on the fragmentation of acetone (Figure 14 ref 3) and trifluoroacetone (Figure 16 ref 3) by Levis et al. The sharp peak at *m/z* 58 belonging to acetone ions and the broad peak at *m/z* 69 belonging to CF_3^+ are characteristics that are clearly present in the acetophenone data (Figure 5 ref 2; Figure 18 ref 3) and indicate the presence of these contaminants. The finding of significant amounts of acetone, and the trifluoroacetone fragment CF_3, indicate that samples from previous experiments remain in their chamber for extended periods of time. Acetone and trifluoroacetone preceded the acetophenone experiment in these articles. This finding suggests a mechanism for the presence of these contaminants in their system without implying the original sample is contaminated. Our results on acetophenone show no peaks at *m/z* 58 or 69. Most importantly, we failed to see the toluene ion (*m/z* 92), which we now suggest was caused in their experiment by an additional contaminant in their chamber. Their inability to find toluene when the experiment was repeated in their laboratory (ref 4, note wrong assignment) supports our assertion. Not surprisingly, we found that the addition of toluene to our sample (2.5% v/v) was sufficient to obtain a toluene ion peak of the same intensity as the C_6H_5CO ion, as observed by Levis et al.[2,3] Even a trace of toluene from a possible previous experiment or from its use for cleaning vacuum chamber components such as o-rings could have accounted for its observation.

In their experiment, the phase-amplitude modulator was placed within the stretcher of the regenerative amplifier, while in our laboratory the phase modulator was located before the regenerative amplifier. The main drawback for placing the modulator within the stretcher is that it could limit the bandwidth of the shaped pulses. Note that details on how the pulses were shaped are of minimal consequence because we are comparing results obtained with transform limited pulses, as indicated in their figures captions (Figure 5a in ref 2; Figure 18 in ref 3). Their article distinguishes between results obtained with 60 fs transform limited pulses from those obtained using the optimization algorithm controlled shaper. For our experiments the laser pulses were characterized and phase distortions are eliminated using MIIPS (see Figure S1).[5] There are no details on how they determined their pulse duration.

In regard to the factor of 4 increase in the production of toluene, we found that toluene undergoes very limited fragmentation under laser irradiation. This explains why pulse shaping would decrease the relative abundance of the larger acetophenone fragment ions in comparison to the toluene molecular ion, as found in their experiments (Figure 21 of ref 3; Figure 5D of ref 2). We note that for all laser conditions in refs 2 and 3, including transform limited pulses, toluene was observed. This is in clear contrast with the absence of toluene for all conditions tested in our laboratory.

Their more recent work indicated minimal changes in the fragmentation pattern of acetophenone as a function of chirp, but a closed-loop experiment with phase and amplitude optimization could double the 105/77 ratio.[4] Their data were obtained with 60 fs pulses (we estimate the range of their chirp to be from −19 000 to +16 000 fs^2). We measured the chirp dependence by introducing a set of 500 chirp values ranging from 0 to 20 000 fs,[2] starting with 35 fs transform limited pulses.[5] In these experiments, the relative yield of *m/z* 105 ions decreases by more than 1 order of magnitude while *m/z* 77 and *m/z* 51 ions experience fewer changes. From our experimental results it is clear that any ratio involving *m/z* 105 ions will change significantly with chirp.

Although the authors allude to experiments carried out on partially deuterated acetophenone $C_6H_5COCD_3$ to confirm the identity of the toluene product, these critical data have not been published in the peer reviewed literature.[2−4] In conclusion, our analysis of the data on acetophenone from ref 4 showed no *m/z* 92 (toluene) ions, and our experiments closely matching the conditions of that experiment confirm this lack of toluene ions. Experiments from our group carried out under the conditions indicated in both refs 2 and 3 showed no *m/z* 92 ions. Experiments carried out under conditions specified by Levis (email correspondence) showed no *m/z* 92 ions. Finally, experiments using a wide range of intensities, pulse durations, and pulse shapes also showed no *m/z* 92 ions (see Figures S10 and S11). The preponderance of the evidence therefore calls into question the laser control of molecular rearrangement reported by Levis et al.[2,3]

Acknowledgment. The findings reported here represent a small detail of a year long study on laser control of chemical reactions that involved more than 16 different samples.[1] We gratefully acknowledge partial financial support from the Chemical Sciences, Geosciences and Biosciences Division, Office of Basic Energy Sciences, Office of Science, U.S. Department of Energy for the study of molecules under high intensity laser fields, and from the NSF (CHE-0500661) supporting our systematic study of laser control of chemical reactions. This work is also partially supported by an STTR subcontract from BioPhotonic Solutions Inc. funded by the US Army Research Office (the content of the information does not necessarily reflect the position or the policy of the Government; no official endorsement should be inferred).

Supporting Information Available: Details of the instrumental and experimental conditions (pulse characterization, focusing, pulse shaping, and absence of space-time coupling) as well as mass spectra obtained under 28 different conditions. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

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JP073970I