Published in final edited form as:

Proc SPIE Int Soc Opt Eng. 2011 August 23; 8173: . doi:10.1117/12.897909.

Control of femtosecond laser driven retro-Diels-Alder-like reaction of dicyclopentadiene

Dipak Kumar Das¹, Tapas Goswami², and Debabrata Goswami^{1,*}

¹Department of Chemistry, Indian Institute of Technology Kanpur, Kanpur-208016, India

²Department of Chemistry, Mudd Building, Stanford, CA 94305-5080, USA

Abstract

Using femtosecond time resolved degenerate pump-probe mass spectrometry coupled with simple linearly chirped frequency modulated pulse, we elucidate that the dynamics of retro-Diels-Alder-like reaction of dicyclopentadiene (DCPD) to cyclopentadiene (CPD) in supersonic molecular beam occurs in ultrafast time scale. Negatively chirped pulse enhances the ion yield of CPD, as compared to positively chirped pulse. This indicates that by changing the frequency (chirp) of the laser pulse we can control the ion yield of a chemical reaction.

Keywords

Time resolved mass spectrometry; chirped pulse; Femtosecond; control

1. INTRODUCTION

Femtosecond time resolved mass spectrometry is one of the most sensitive and reliable method for probing ultrafast reaction dynamics of molecules. Control of chemical reaction is a long-sought-after goal for chemists. Certain successful demonstrations have been made over the past decade through the detection of molecular fragmentation patterns using an adaptive approach of the ultrafast laser pulse shaping technique [1, 2]. One of the simplest pulse modulation concepts is frequency chirping [3]. Control of fragmentation and chemical reactions with simple linear chirped pulse as a control scheme has become an active field of research in recent years [4, 5].

Discovered in the 1920s [6], Diels-Alder and its reverse process remains as one of the most widely used methods in synthetic chemistry. The mechanism and the real time dynamics study of this reversible process has become one of the most active field of research in recent years [7-9]. However any attempt to control such process is yet to be reported. We present here our results on the photochemical control of a reversible retro-Diels-Alder-like reaction. We specifically explore the effect of chirping femtosecond laser pulses on the control of retro-Diels-Alder-like reaction of dicyclopentadiene (DCPD). DCPD is the product of the retro-Diels-Alder-like reaction of two cyclopentadiene (CPD) molecules (Scheme 1):

Scheme 1.

Diels-Alder and its reverse, retro-Diels-Alder-like reaction under discussion.

We present here a femtosecond laser induced study on the photo fragmentation of DCPD. We specifically refer this as the retro-Diels-Alder-like reaction since this photochemical process accesses the excited state pathway, which is unlike the actual Diels-Alder class of reactions that proceed only through the ground-state.

2. EXPERIMENTAL

Our experimental setup [5] consisting of a linear time of flight mass spectrometer (TOFMS) interfaced with a commercially available Ti: Sapphire multipass amplifier (Odin, Quantronix Inc.) operating at 800 nm with 50 fs full-width at half maximum (FWHM) pulses at repetition rate of 1 kHz. Linearly frequency modulated ultrafast laser pulses (Chirped pulses) were generated from our suitably modified compressor setup for the amplified laser system. By increasing the inter grating distance of the compressor relative to the optimum position for minimum pulse duration of 50 fs, we generate a pulse whose leading edge is bluer than the trailing edge (negative chirping). Conversely by decreasing the inter-grating distance, we obtain a pulse whose leading edge is redder than the trailing edge (positive chirping). Pulse duration of transform-limited (TL) pulse was measured using a homemade field autocorrelator. The chirped pulses were characterized by using second harmonic frequency resolved optical grating (SHG-FROG) technique by using a 0.1 mm type-1 barium-beta borate (BBO) crystal.

As shown in the experimental setup in figure 2, the molecular beam and laser beams crossed at the laser focus. The incident laser intensity was varied by using a variable neutral density (ND) filter, keeping the beam focusing geometry and beam diameter constant. For collinear degenerate pump-probe study the laser beam was split to provide pump and probe beam by using a ultrafast 70:30 beam splitter and then probe beam is allow to travel through a computer controlled motorized delay line and then two beams were specially combined by an another 70:30 beam splitter, the laser pulses are then focused by using 50 cm focal length lens onto the supersonic molecular beam containing a linear TOFMS. Our molecular beam chamber consists of three different chambers with different pumping to attain a supersonic molecular beam region, laser interaction region and mass detection region respectively. The pressure in the ionization chamber during the experiment was kept at 10^{-7} torr. During the experiment the pump beam intensity was kept smaller compared to the probe beam.

The molecular beam was generated by the expansion of DCPD sample (98%; Sigma Aldrich) at room temperature, which was used without further purification. This was seeded in a He carrier gas at 2 atm. through a nozzle orifice having 100 μm diameter and a skimmer with 1 mm diameter. The fragment ions are accelerated by a Wiley-McLaren type time of flight mass spectrometer and detected by using an 18 mm dual micro-channel plate (MCP) detector that was coupled to a 1 GHz digital oscilloscope (Lecroy 6100A). Mass spectra were typically averaged over 200 laser shots. Using our final experimental setup as shown in figure 2, we can conduct photo chemical control as well as one color pump-probe study.

3. RESULTS

The mass spectra of DCPD with transform-limited pulse at FWHM = 50 fs with 203 μJ /pulse energy is shown in figure 3(a). The threshold laser intensity that we need for detecting any mass spectroscopic signal was 180 μJ /pulse energy and the detected mass spectra was dominated by two fragments having m/z values of 66 and 132, respectively. At laser energies of 360 μJ /pulse and beyond (figures 3(b) and 3(c)) multiple mass fragmentations occur that results in the formation of DCPD^+ and CPD^+ . At 360 μJ /pulse energy and beyond multiple mass fragmentation occurs.

Next, we chirp the pulse and compare the results of the time of flight mass spectra (TOFMS) of DCPD at different amounts of linearly chirped pulses with respect to the unchirped ultrafast laser pulses at the constant average energy. We compare the corresponding peaks in the mass spectra of DCPD^+ and CPD^+ , respectively, by calculating their respective integrals under the ion peaks. The value of chirped parameter was calculated by using the equation,

$\tau^2 = \tau_0^2 + \left[\frac{4\beta \ln 2}{\tau^2} \right]^2$, where β is the linear chirp coefficient, τ is the pulse duration of the chirped laser pulse and τ_0 is the pulse duration of the TL pulse. The calculated value of chirp is within $\pm 9\%$.

We implement the degenerate time-resolved pump-probe method for studying inter-conversion dynamics of DCPD to CPD. The pump laser pulse excites DCPD, which starts to produce the molecular ion. After a variable delay the probe laser takes a snapshot of the evolving system. The ions produced by the laser are detected by a linear TOFMS. Figure 4 shows the transient of the DCPD^+ and CPD^+ . All the transients are measured with attenuated pump and probe laser beams, where each of the laser pulses alone produces negligible amount of ions. Under these experimental conditions, the observed dynamics have to occur where the probe laser induces the reactions and further ionization.

The formation of DCPD^+ and the photochemical reaction product CPD^+ are expected to be two different temporally evolving channels, which is supported by the investigations of Zewail *et. al.* [4]. This justifies our observation that the transient signal of the CPD^+ reaction fragment is different from that of DCPD^+ . This also indicates that the dynamics we are studying is distinct dynamics of the neutrals and is not due to fragmentation of the parent ion. Furthermore, this confirms that the system we are attempting to control by chirping of the photochemical laser pulse is the product yield of CPD^+ resulting from the photochemical reaction of DCPD, and not from the fragmentation of DCPD^+ .

Now, the product yield distribution for a chemical reaction depends upon the coupling between the potential energy surfaces participation in the chemical reaction, as well as the characteristics of the interacting laser field, such as , its frequency, pulse duration, intensity and chirp. Quantum mechanical wavepacket $\psi(t)$ produced through the absorption of an

ultrafast laser pulse is expressed as $\psi_n(t) = \sum_n a_n e^{-iE_n t/\hbar} \Phi_n$, where E_n is the Eigen value and Φ_n is the Eigen Function of each level n . The exponential part remains same for all states when it is excited with TL pulses or unchirped pulses. However using the chirped pulse excitation therefore, influences wavepacket shape and dynamics. This in turn, changes the photochemical outcome and as discusses earlier [10, 11] as a chemical reaction control.

As we increase the pulse duration with chirp, the relative yield of CPD^+ arising out of retro-Diels-Alder-like reaction of DCPD changes. The peak intensity of CPD^+ is high for negatively chirped pulses as compared to the positively chirped pulses. The peak intensity of DCPD⁺ remains the same for a fixed chirped case.

Similar observations have been found earlier in the case of enhancement of I_2 elimination from CH_2I_2 [10] and enhancement of multi-photon absorption in molecular iodine [11] by chirped pulse. Yakovle *et. al.* [11] were able to explain their observed results by quantum mechanical calculation which shows that the wavepacket following effect is one of the reasonable arguments behind the enhancement of three photon absorption with positively chirped pulses. Since the potential energy surfaces involved in our particular chemical reaction is unknown and no potential energy surface can be calculated for such large systems with sufficient accuracy, an accurate description of the effect is not possible to be offered presently. However, it can be conjectured that in analogy to the previous experiments where a red blue sequence of photon interaction starts and ends at different points on the potential energy surface as compared to a blue-red sequence which could possibly lead to a relatively high enhancement of negative chirp fragment due to a better overlap between pump-pump or pump-dump pulse as compared to that of the TL pulse case.

Though this may look like a plausible explanation, it is important to note that the reaction product in our particular case arises from the ground state reaction coordinate. Only the pump-dump scheme would, therefore, lead eventually product fragment ion. Consequently, all the discussions for the wavepacket overlap have to essentially translate to a constructive overlap of the pump-dump pulse to result back to the ground potential energy state from the initially excited state potential.

Suitably overlapped pump-dump pulse may promote return of the excited DCPD molecule to the ground vibrationally hot state of DCPD and preferentially yield CPD, which may then be followed by a four photon ionization resulting in the ion yield as observed. The initial photon mediated pump-dump process that results in the generation of the vibrationally hot ground state precursor must be the critical initial condition of the reaction coordinate that explains the major effect of the negatively chirped pulse as compared to the positively chirped pulses. There may be some effect of chirp on the four photon ionization process of the molecular ion and the inter-conversion into the CPD product as well. However such

effects would fail to bring about the observed distinction in the behavior of DCPD ion yield as compared to that of the CPD ion yield.

4. CONCLUSION

We have demonstrated the importance of phase structure of a femtosecond pulse in affecting the retro-Diels-Alder-like reaction, which is shown to occur on the ultrafast time scale using one color femtosecond pump-probe technique. Chirping of ultrafast laser pulse enhance the yield of CPD⁺, the enhancement of CPD⁺ is an order of magnitude in case of negatively chirped pulse as compared to that of the positively chirped pulse.

ACKNOWLEDGEMENTS

D.K.D. and T.G. thanks CSIR and UGC respectively for awarding fellowships. D.G. acknowledges the support of this work by a Swarnajayanti Fellowship in Chemical Sciences from the Department of Science and technology (DST), India and a Wellcome Trust (UK) International senior Research Fellowship.

REFERENCES

- [1]. Assian A, Baumert T, Berget M, Brixner T, Kiefer B, Sayfried V, Strehle M, Gerber G. Control of Chemical Reactions by Feedback-Optimized Pulse-Shaped Femtosecond Laser Pulses. *Science*. 1998; 282:919–922. [PubMed: 9794756]
- [2]. Levis RJ, Menkir GM, Rabitz H. Selective Bond Dissociation and Rearrangement With Optimally Tailored , Strong-Field Laser Pulses. *Science*. 2001; 292:709–713. [PubMed: 11283357]
- [3]. Milenger JS, Gandhi SR, Hariharan A, Goswami D, warren WS. Adiabatic population transfer with frequency-swept laser pulses. *J. Chem. Phys.* 1994; 101:6439–6454.
- [4]. Lozovoy VV, Zhu X, Gunatane TC, Harris DA, Harris JC, Shane JC, Dantus M. Control of Molecular Fragmentation Using Shaped Femtosecond Pulses. *J. Phys. Chem. A*. 2008; 112:3789–3812. [PubMed: 18433144]
- [5]. Goswami T, Kumar SKK, Dutta A, Goswami D. Control of laser induced molecular fragmentation of n-propyl benzene using chirped femtosecond laser pulses. *Chem. Phys.* 2009; 360:47–52. [PubMed: 19696899]
- [6]. Diels O, Alder K. Syntheses in the hydroaromatic series.1. addition of “diene” hydrocarbons. *Justus Liebigs Ann. Chem.* 1928; 460:98–122.
- [7]. Horn BA, Herek JL, Zewail AH. Retro-Diels-Alder Femtosecond Reaction Dynamics. *J. Am. Chem. Soc.* 1996; 118:8755–8756.
- [8]. Diau EW–G, De Feyter S, Zewail AH. Femtosecond Dynamics of retro-Diels-Alder Reactions: the concept of concertedness. *Chem. Phys. Letts.* 1999; 304:134–144.
- [9]. De Feyter S, Diau EW–G, Scala AA, Zewail AH. Femtosecond dynamics of diradicals: transition states , entropic configurations and stereochemistry. *Chem. Phys. Letts.* 1999; 303:249–260.
- [10]. Pastrik I, Brown EJ, Zhang Q, Dantus M. Quantum control of the yield of a chemical reaction. *J. Chem. Phys.* 1998; 108:4375–4378.
- [11]. Yakovlev VV, Bardeen CJ, Che J, Cao J, Wilson KR. Chirped pulse enhancement of multiphoton absorption in molecular iodine. *J. Chem. Phys.* 1998; 108:2309–2313.

Figure 2.
Schematic experimental setup showing amplified chirped pulse interaction with supersonic molecular beam chamber.

Figure 3.

Mass spectrum of DCPD with FWHM = 50 fs that is (a) transform-limited. When the same pulses are chirped such that the pulse FWHM = 445 fs (chirp parameter, β value of (b) -8064 fs^2 and (c) $+8064 \text{ fs}^2$) mass spectra of DCPD.

Figure 4.
Degenerate pump-probe transient spectra at 800 nm of DCPD⁺ and CPD⁺