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Chirp and polarization control of femtosecond molecular fragmentation

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Abstract

We explore the simultaneous effect of chirp and polarization as the two control parameters for non-resonant photo-dissociation of *n*-propyl benzene. Experiments performed over a wide range of laser intensities show that these two control knobs behave mutually exclusively. Specifically, for the coherently enhanced fragments ($C_3H_3^+$, $C_5H_5^+$) with negatively chirped pulses and $C_6H_5^+$ with positively chirped pulses, polarization effect is the same as compared to that in the case of transform-limited pulses. Though a change in polarization affects the overall fragmentation efficiency, the fragmentation pattern of *n*-propyl benzene molecule remains unaffected in contrast to the chirp case.

Keywords

Photodissociation; Control; Femtochemistry; Chirp pulses

1. Introduction

Study of control of photo-fragmentation and photochemical reactions with different parameters or ‘control knobs’ of the interacting laser pulse, such as, the temporal shape [1–4], frequency content [5], intensity [6, 7], polarization [8, 9], etc., is of great interest due to its diverse applications ranging from fabrication of gene chips, microelectronic lithography or photodynamic therapy¹ to even quantum information processing [10, 11]. Femtosecond laser pulse photo-fragmentation experiments with varying laser polarization or instantaneous phase characteristics (chirp) have evolved polarization and chirp as the two important ‘control knobs’ affecting the fragmentation under the fixed conditions of excitation wavelength, laser intensity, and beam focusing geometry [3, 8, 9, 12, 13].

The fragmentation processes in polyatomic molecules induced by intense laser field often exhibit sensitive dependence on either the chirp [3, 12, 13] or the polarization [8, 9, 14] of the laser field. Depending on the change in the sign of the chirped laser pulses, fragmentation could be either enhanced or suppressed. We have recently reported some coherently enhanced fragmentation pathway of *n*-propyl benzene using chirped femtosecond laser pulses [12]. Similarly, a vast amount of reported study on the effect of polarization on fragmentation shows a substantial suppression of fragmentation channel when polarization is altered from linear to circular for non-resonant dissociation [15–22]. Such suppression with circular polarization has been associated with electron re-scattering or re-collision (ERC) [23] though the molecular fragmentation pattern has been unaffected by laser polarization [24, 25].

A simultaneous effect of these two ‘control knobs’ of polarization and chirp are yet to be explored. In this paper, we experimentally study the simultaneous effect of chirp and polarization ‘control knobs’ on the non-resonant photofragmentation of *n*-propyl benzene. Though our main focus has been to study whether the polarization of the laser pulse affects our observed change in the fragmentation pattern with chirped femtosecond laser pulses of *n*-propyl benzene, our experiments also enable us to explore the importance of the various possible mechanisms of the fragmentation process.

2. Experimental details

We use a Ti:Sapphire multipass amplified laser system (Odin, Quantronix Inc.), which operates at 800 nm with 50 fs FWHM pulses at 1 kHz with energy of ~1 mJ. Our suitably modified compressor in this amplified laser system enables easy generation of chirped ultrafast laser pulses. As we increase the spacing between compressor gratings relative to the optimum position for minimum pulse duration of 50 fs, we generate a negatively chirped pulse. Conversely, we obtain the positively chirped pulse by decreasing the inter-grating distance. Linear Chirping refers to the process of arranging the frequency components linearly within the bandwidth of the laser pulses. For the negatively chirped pulse the leading edge of the pulse is blue shifted and the trailing edge is red shifted while positively chirped pulse corresponds to the opposite effect. Pulse durations for all such pulses were measured using a home-made auto-correlator. Linear chirp coefficient

$\left(\beta = \tau_0 \sqrt{(\tau^2 - \tau_0^2) / 4 \ln 2} \right)$ can be calculated if the pulse duration of the unchirped pulse (τ_0) and chirped pulses (τ) is known. The laser polarization is varied from linear to circular by using a quarter-wave plate (Thorlabs, AQWP05 M-980) and from parallel to perpendicular by using a half-wave plate (Thorlabs, AHWP05 M-980).

The laser pulses are then focused with a 50 cm focal length lens on a skimmed supersonic molecular beam of *n*-propyl benzene at the center of the two electrical plates (repeller and extraction) of the time of flight chamber. The design of our molecular beam setup (Fig. 1) consists of three chambers with differential pumping by turbo pumps. The three chambers were designed with differential pumping to attain a supersonic jet expansion region, a laser interaction region and a mass detection region, respectively. The source chamber or the supersonic jet region is pumped by 2,000 ls^{-1} turbo molecular pump (Varian Turbo-V2 K-G). The ionization chamber (or the buffer chamber), which is where the laser interaction occurs, is pumped by a 500 ls^{-1} turbo pump (Varian Turbo-V 551 Navigator). Finally, the mass detection region is pumped by a 300 ls^{-1} turbo pump (Varian Turbo-V 301 Navigator). The pressure in the ionization chamber during the experiment was kept at 10^{-7} Torr (base pressure of 5×10^{-9} Torr). A pulsed valve (Series 9, General Valve) of 0.5-mm diameter operating at 10 Hz repetition rate and a skimmer of 1-mm diameter were used to introduce the supersonic molecular beam into the laser interaction region, where it is exposed to the intense laser. The pulsed valve is placed on an XYZ stage (MDC Inc.) to precisely align the pulsed valve in line with the skimmer. The pulse duration of the molecular beam is kept at 100 μs . The molecular beam and laser pulses are synchronized by a delay generator. The *n*-propyl benzene sample at room temperature was used without further purification (98 %; Sigma Aldrich) and was seeded in Helium at 2 atm backing pressure. The mass spectra were recorded with a Wiley–McLaren type linear time of flight mass spectrometer. The ions are detected using an 18-mm dual micro-channel plate (MCP) detector coupled to a 1 GHz digital oscilloscope (Lecroy 6100A). Mass spectra were typically averaged over 500 laser shots.

3. Results and discussion

Using the above experimental set up, we have recently shown that the phase characteristics of the laser field play a very important role in the fragmentation of *n*-propyl benzene [12]. We showed a sufficient difference in the fragmentation pattern of *n*-propyl benzene when we use chirped pulse as compared to the transform-limited pulse. Negatively chirped pulse enhances the relative yield of $C_3H_3^+$ and $C_5H_5^+$ fragments while the relative yield of the $C_6H_5^+$ fragment increases with positively chirped pulse. The possible reasons behind the enhancement of the relative yield of the smaller fragments can be the better overlap for the particular fragments since red–blue sequence (negatively chirped pulse) starts and ends at different potential energy surface than the blue red sequence (positively chirped pulse) [12].

Here, we further the study by including the effect of polarization of the laser pulses on the fragmentation pattern of *n*-propyl benzene both independently as well as when the laser pulses are also simultaneously chirped. For all such studies, we recorded the mass spectra of *n*-propyl benzene using linearly chirped and unchirped laser pulses with varying angle of the quarter-wave plate. The average energy (~200 mW) of the laser pulses was kept constant using a variable ND-filter. We then compare the mass spectra by calculating their respective integrals under the peak. No coupling of these two parameters is observed. For both unchirped and chirped cases fragmentation channels are suppressed when we alter the polarization from linear to circular (Fig. 2). In Fig. 3, we also compared the fragmentation pattern to the intensity of the specific polarization component, which shows a strong correlation to the intensity of the laser.

All the fragmentation channels that were enhanced with chirped pulses were suppressed to roughly the same extent as compared to the unchirped pulse case (Fig. 4). So the fragmentation pattern is unchanged if we alter the polarization at any particular chirp of the laser pulse. Relative ratios of the fragment ions are essentially similar. When we change the polarization from linearly polarized light (LP) to circularly polarized light (CP), molecular ion yield is suppressed by a factor of 0.52, as $\frac{I_{CP}}{I_{LP}} = \frac{[M^+]_{CP}}{[M^+]_{LP}} = 0.52$. Up to a certain amount of chirp, this ratio, $\frac{I_{CP}}{I_{LP}}$, is almost constant, however, when the laser pulses are highly chirped, $\frac{I_{CP}}{I_{LP}}$ increases. This can be due to the lowering of laser peak intensity at high chirps. Nevertheless, the oscillatory pattern of the ion yield as a function of polarization angle (i.e., at different ellipticity of the laser beam) prevails regardless of the chirp amount.

In both directions of the chirp, observed variation in the ion yield is the same within our signal to noise ratio with an order of the fragmentation of *n*-propyl benzene to be ~6 photon process as has been previously reported [26].

The main factors responsible for changing the dynamics of the field molecule interaction [17, 18] are: (1) the varying directions of the electric field vector of the interacting laser radiation, (2) the differing electric field amplitude of the circular to that of the linear polarization at the same laser intensity, and (3) the polarization state dependence of the angular momentum selection rule. These three factors, in fact, are also present in case of atomic ionization. However, in the case of molecular ionization additional factors of the field molecule interaction need to be considered, such as: (4) the polarization tensors in the molecule that might lead to spatial alignment, specifically in case of linear polarization, (5) the angle between the induced dipole in the molecule and the electric field of the incident light, (6) the rovibrational couplings in the electronic states that influence inter-atomic distances, (7) the effect of enhanced ionization, and (8) the differences in the quantum descriptions of the electronic states that are excited, owing to the different angular momentum selection rules [17, 18]. Because of all these factors behind polarization

dependent molecular dynamics in intense light field, finding the actual reason behind it, is very difficult but at the same time interesting.

Given the laser intensities used in our experiments, we would expect to modulate the probability of electron nuclei-collisions in analogy to the high harmonic generation process by changing the polarization from linear to circular [16]. However, we have observed that these changes in polarization do not affect the fragmentation pattern (Fig. 3). This suggests that ERC does not play a major role in determining the fragmentation pattern in our experiments, which implies that electron nuclei collisions are not needed for the electron to transfer energy to the molecule. Instead, our results prove that the phase of the laser pulse plays a very important role in determining fragmentation pattern whereas the polarization does not play any role at our experimental condition. In fact, we find that the affect of phase characteristics and the polarization state of the interacting laser pulse on the fragmentation dynamics of *n*-propyl benzene is mutually exclusive in nature. This follows from the fact that the fragmentation pattern of *n*-propyl benzene is not changing from linear to circular: it is only the total fragment ion yield that is being suppressed, which further reinforces our suggestion that ERC does not play a major role in determining the fragmentation pattern in our experiments or that electron–nuclei collisions are not needed for the electron to transfer energy to the molecule.

Thus, our results essentially emphasize the fact that the modulation of the fragmentation pattern by the chirped pulse is governed only by the phase characteristics of the laser pulse. Some of the other factors that may be responsible for the suppression of fragmentation by a factor of 0.52 from linear to circular are: (a) the electric field amplitude differ from circular to linear at the same laser intensity, (b) the polarization tensors in the molecule might lead to spatial alignment, specifically in the case of linear polarization, and (c) the dependence of the ionization rate on the angle between induced dipole in the molecule and the electric field of the incident laser beam.

In this particular study, chirp parameter acts as a control knob at the molecular level affecting the fragmentation pattern, whereas the laser polarization acts as a knob to spatially align the molecule. Furthermore, the chirped pulse controls the fragmentation of molecule in the same manner when the molecules are aligned by polarization of the laser pulse and when it is not aligned.

4. Conclusions

Our experimental data reveals that the two important control parameters chirp and polarization of the ultrafast laser pulse are mutually exclusive in nature. Polarization does not change the fragmentation pattern which is changed by chirp of the laser pulse, rather it only decrease the dissociation efficiency. The dissociation is suppressed when the polarization is altered from linear to circular. Polarization does not play a major role in deciding the fragmentation pattern.

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Fig. 1. Schematic diagram of molecular beam chamber with linear time of flight mass spectrometer setup

Fig. 2.

a Mass spectra of *n*-propyl benzene when laser beam is linearly and circularly polarized light excitation with transform limited ($\beta = 0 \text{ fs}^2$) pulses. **b** Mass spectra of *n*-propyl benzene when laser beam is linearly and circularly polarized light excitation with negatively chirped ($\beta = -8,064 \text{ fs}^2$) where there is an enhancement of C_3H_3^+ and C_5H_5^+ fragment ion yield. **c** Mass spectra of *n*-propyl benzene when laser beam is linearly and circularly polarized light excitation with positively chirped ($\beta = +6,246 \text{ fs}^2$) where there is an enhancement of C_6H_5^+ fragment ion yield

Fig. 3.

Normalized variation of different fragment ion yield with polarization angle of the quarter-wave plate at constant average laser power. This variation is compared to the measure of the linear component of the constant laser power after the quarter-wave plate at a fixed chirp value by using a calcite polarizer in place of the sample

Fig. 4. Normalized variation of C_3H_3^+ ion yield with polarization angle at different amount of chirp of the laser pulse