

Controlling neutral fragmentation yields of methane by femtosecond laser pulses

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We demonstrate the control of neutral fragmentation of methane (CH₄) induced by a Ti:sapphire intense laser pulse (800 nm, 40 fs) by using a pump-probe spectroscopy. Enhancement of the fluorescence emission from the neutral radical CH (A²Δ → X²Π) induced by the intense laser field (~10¹⁴ W/cm²) is observed when the wavelength of the probe laser pulse is tuned to 400 nm. The phenomena are explained based on excitation enhancement of the super-excited state of the parent molecule resulting in an increase in neutral dissociation of the methane molecules.

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The interaction of molecules with femtosecond intense laser fields has been studied for many years^[1]. One of the major goals in such studies is to find ways to control the photo-induced chemical reactions by tailoring/shaping laser pulses^[2-4]. With the excitation of an intense field at intensity of ~10¹²–10¹⁴ W/cm², molecules undergo a variety of dynamical processes, in which neutral fragmentation can occur^[5,6]. Recently, the fluorescence emissions from CH (A²Δ, B²Σ⁻, C²Σ⁺), C₂ (d³Π_g), and H were observed from the fragmentation of the parent molecules including methane, ethylene, and 1-butene in intense laser fields (~10¹⁴ W/cm²)^[7]. It was suggested that the neutral fragments of CH and H results from neutral dissociation of molecules through super-excited states (SEs)^[8-10], which are interpreted as those neutral Rydberg states of molecule with energies higher than the ionization potential (IP) under field-free conditions^[11]. More recently, it was theoretically demonstrated that in the presence of intense laser fields the instantaneous potential energy curves of some SEs of methane would be energetically pushed down below the IP, leading to the neutral dissociation along the CH₄ → CH₂ + 2H paths with subsequent reaction of CH₂ → CH + H^[12].

On the other hand, when powerful femtosecond laser pulses propagate in air, a high laser intensity of about 5 × 10¹³ W/cm² can be achieved over a long distance from a so-called femtosecond laser filamentation process^[13], which appears as a result of the dynamic interplay between Kerr self-focusing and defocusing by the plasma produced by multiphoton/tunnel ionization of air molecules^[14]. This intensity is high enough to induce many nonlinear processes such as terahertz radiation and remote air lasing^[15,16]. In particular, neutral dissociation

of impurity molecules in air in such high intensity may result in the characteristic fluorescence emission from the fragments of the impurities, which can be used as fingerprint for identifying trace gases in the atmosphere. Since the detection sensitivity is limited in general by the efficiency of generation of the fluorescence^[17], it is thus of great interest in seeking a feasible strategy to enhance the yield of neutral excited fragments of molecules induced by intense laser fields^[18,19].

Recently, it was demonstrated that the fluorescence signal from molecules (such as CH₄, O₂, NO, and H₂) induced by femtosecond 800 nm laser pulses can be partially depleted when a second infrared laser pulse at λ ~ 1.3 μm was applied as the probe^[8-10,20]. Here we employ methane molecules as the target, and study its fluorescence emissions induced by strong 800 nm laser fields in a pump-probe scheme with a 400 nm blue light as the probe. Contrary to using the infrared (λ ~ 1.3 μm) as the probe, we observed a significant increase in the fluorescence from the A²Δ → X²Π transition of CH. The completely opposite effect on the CH product by the blue and infrared probe laser pulses can be explained based on the competition between the excitation enhancement and de-excitation of the SEs of CH₄.

The experiment was conducted using a Ti:sapphire femtosecond laser system. The experimental schematic diagram is depicted in Fig. 1. The output of the laser pulses was centered at 800 nm with a 23 nm bandwidth (full-width at half-maximum) and the diameter of the beam was about 5 mm (at 1/e² level of intensity). The laser beam was split into two parts by a 50/50 beam splitter. One arm of the beam was used as the pump with a pulse energy of ~900 μJ and a pulse duration of ~42 fs. The other arm was frequency

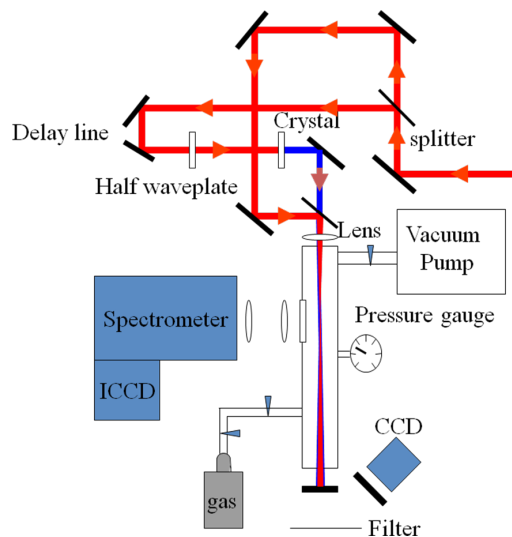


Fig. 1. Experimental setup.

doubled in a potassium dihydrogen phosphate (KDP) crystal to generate blue probe pulses at 400 nm with a pulse energy of $\sim 30 \mu\text{J}$ and a pulse duration of $\sim 100\text{--}200$ fs. The probe pulse was arranged to have a horizontal polarization parallel to that of the pump beam. A variable delay line with a spatial resolution of 40 nm was inserted into the probe beam to make a precise temporal delay between the pump and probe pulses. The spatial superposition of these two pulses was checked with a far-field measurement, and the temporal superposition was examined by observing the refraction pattern of the 400 nm probe beam induced by the pump laser-induced plasma. Both the pump and probe beams were focused by a fused silica lens ($f = 30$ cm) into a vacuum chamber filled with CH_4 at 20 Torr. The thickness of the input fused silica window was 6 mm and the distance between the focusing lens and the input window of the vacuum chamber was 2 cm.

The induced fluorescence signal was collected at a right angle to the laser propagation direction and dispersed by a spectrometer (Acton Research Corp., Spectrapro-500i) equipped both with a gated intensified charge coupled device (ICCD; Princeton instruments Pi-Max 512) and a microchannel plate photomultiplier tube (Hamamatsu R5916U-52). A Tektronix Model TDS 7254 oscilloscope with a bandwidth of 2.5 GHz was used to record and average the signals from the photomultiplier tube.

Figure 2 shows a typical femtosecond laser-induced fluorescence spectrum of CH_4 in the spectral region of 300–700 nm. The spectrum was obtained with the excitation of the pump pulse only, that is, the probe pulse was blocked. The main spectral lines were assigned to CH ($A^2\Delta$, $B^2\Sigma^-$, $C^2\Sigma^- \rightarrow X^2\Pi$) and C_2 (Swan band)^[7]. Here we can undoubtedly conclude that the products of C_2 are due to the collisions among the induced fragments or ionization products, based on the fact that

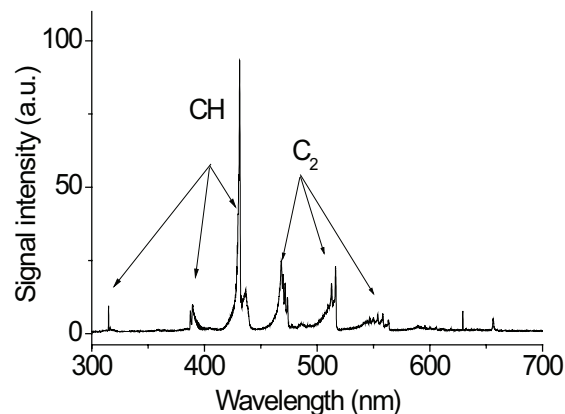


Fig. 2. Femtosecond laser-induced fluorescence spectra of CH_4 . The ICCD gate width was set to $1 \mu\text{s}$ and the ICCD delay time $t = -10$ ns (note that the laser pulse arrives in the interaction region at $t = 0$). The data were averaged over 200 shots.

the C–C bond is absent in the parent molecule CH_4 . As for CH, it has been previously attributed to the neutral dissociation of CH_4 through the SESs^[7,8,12]. Here we will only focus our attention on the fluorescence emission from the $A^2\Delta \rightarrow X^2\Pi$ transition of CH at 431 nm using the femtosecond pump–probe technique.

As shown in Fig. 3, when the frequency doubled 400 nm probe pulses was used, an unambiguous enhancement of the fluorescence was observed (rectangles) at the delay time of $\Delta t \sim 0$ between the pump and probe. For comparison, the data obtained only with the excitation of the pump pulse are also illustrated in Fig. 3 (circles). It should be pointed out that with only the single 400 nm laser excitation, no fluorescence can be observed. The lower curve in Fig. 3 (triangles) is

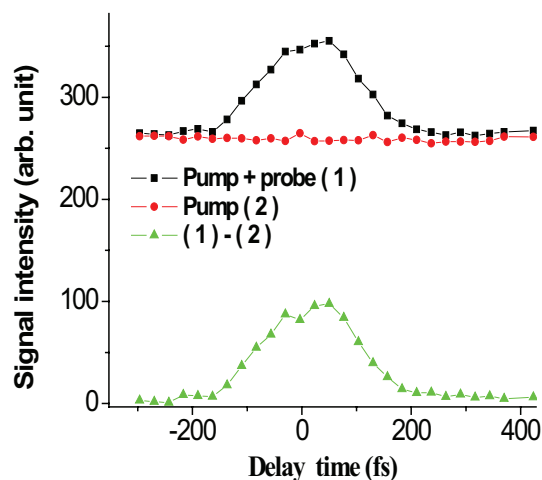


Fig. 3. Fluorescence signal emitted from the $A^2\Delta - X^2\Delta$ transition of CH at 431.2 nm as a function of the delay time between the 800 nm pump and 400 nm probe pulses. The circular points were obtained with the same experimental condition as the rectangular ones, except the probe laser was blocked. The lower curve is the subtraction of (1) from (2).

the subtraction of (1) from (2). The data were averaged over 100 laser shots and the fluorescence signals were integrated within a time interval of 700 ns, in order to add up all the fluorescence in the temporal domain. The pressure in this measurement was 20 Torr. In such condition, a signal enhancement of $\sim 32\%$ is observed in Fig. 3 where the enhancement is defined as the ratio $(S_{\text{pump+probe}} - S_{\text{pump}})/S_{\text{pump}}$, where the numerator is the signal difference at the delay time $t = 0$ between the signals recorded in the presence of the probe and in the absence of the probe pulses and the denominator is the signal recorded only with the excitation of the pump pulse. The fluctuation of the data reflects the stability of our laser system. It should be pointed out that the enhancement of the signal is sensitive to the alignment of the pump and probe pulses and fluctuates in day-to-day measurements.

This result is in contrast to our previous observation that a $\sim 6\%$ depletion of the CH ($A^2\Delta \rightarrow X^2\Pi$) fluorescence signal was obtained when an infrared $1.3 \mu\text{m}$ probe pulse was applied^[8]. The completely inverse effect of the infrared $1.3 \mu\text{m}$ and the blue 400 nm probe pulses on the CH fluorescence may be understood as follows. The 800 nm pump pulse first populates the SESs of CH_4 by multiphoton excitation, as suggested by the fact that the fluorescence shows a 10-photon nonlinear dependence on the pump laser intensity^[7]. In such a strong laser field, resonance-enhanced ionization of the SES's would readily occur and neutral dissociation would become much less probable. However, in the strong broadband radiation (femtosecond laser pulse), there is a probability that the continuum would be coupled to a neighboring state of the SES, inducing a downward transition through a Raman-type process resulting in a coherent re-population of the SESs (see Fig. 4(a)). A further up transition from the SES back into the continuum could in principle occur again

by absorbing another photon of the laser field. Such coherent processes would result in an interference of the transitions into the continuum from different SESs related to the same electron wave. The consequence is some population of the SES would be left behind after the interaction (population trapping). This population trapping process would reduce the ionization rate and leave a significant population in the SESs^[20,21].

On the other hand, since the CH_4 molecule lying on its SESs will automatically undergo a non-radiative decay either by autoionization or by neutral dissociation^[11,22], a second pulse probe with a lower photon energy would de-excite the CH_4 molecule away from the SESs, leading to a depletion of the SESs (see Fig. 4(d)). Since the second probe laser pulse has lower photon energy than the 800 nm laser light and its intensity is much weaker than the pump laser, it cannot enhance the population of the SESs of methane. However, in the case of the 400 nm probe laser pulse, since the 400 nm light has a photon energy twice that of the 800 nm pump pulse, even though the de-excitation of the SESs can occur (Figs. 4(b) and (c)), the 400 nm probe pulse might induce an excitation enhancement of the SESs of CH_4 (see Fig. 4(e) with population trapping). This would result in more fragmentation, hence, fluorescence enhancement. That is, there seems to exist a competition between the excitation enhancement (Fig. 4(e)) and the destruction of the SESs by the 400 nm probe pulse (Figs. 4(b) and (c)). Our experimental results indicate that the former mechanism dominates.

Furthermore, the 400 nm photon with a broad bandwidth can be in near resonance with the transition $X^2\Pi \rightarrow A^2\Delta$ (i.e., absorption), which might populate the $A^2\Delta$ state of CH radical from $X^2\Pi$ (after the fluorescence decay) and lead to the fluorescence enhancement. However, the enhancement profile is about 200 fs (Fig. 3). This time scale is much shorter than the

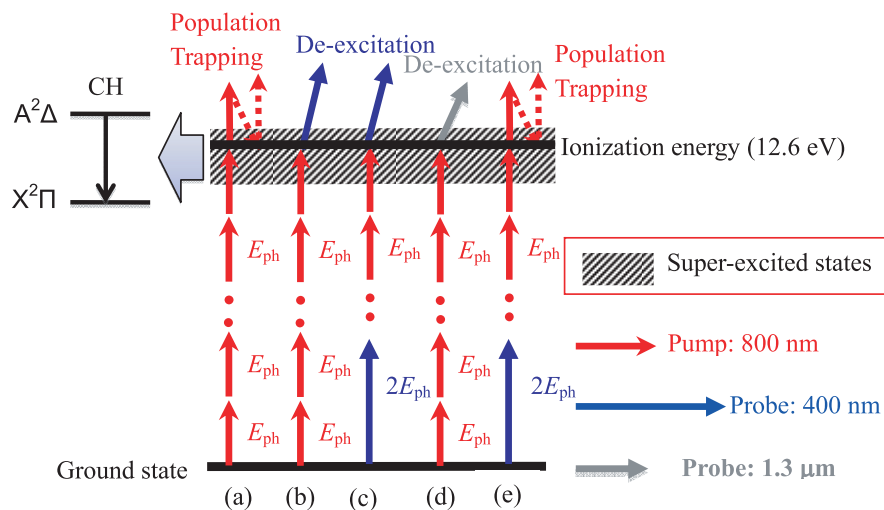


Fig. 4. Schematic of the pump-probe measurement with the 800 nm laser (red) as the pump and the 400 nm (blue) or infrared 1338 nm (gray) laser as the probe.

lifetime of the $A^2\Delta$ state which is in the nanosecond domain. That is to say, within 200 fs, there was not much population in the $X^2\Pi$ coming from the $A^2\Delta$ yet. Thus, this possibility can be neglected.

In conclusion, we study the fluorescence spectroscopy of CH_4 induced by a femtosecond intense laser field. By probing the fluorescence emission from the $A^2\Delta \rightarrow X^2\Pi$ transition of CH as the decay time between the Ti:sapphire 800 nm pump and the blue 400 nm probe pulse, a significant enhancement is observed. This result is in contrast to that obtained by using the infrared laser at $\sim 1.3 \mu m$ as the probe, in which a significant reduction of the fluorescence emission is demonstrated. The completely opposite effect on the CH product by the laser pulse with different photon energy may represent a new strategy for controlling chemical reactions in intense laser fields. Meanwhile, more theoretical work is needed to elucidate the detailed physical process of this interesting phenomenon of ultrafast laser interaction with molecules.

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