IOP Publishing Journal of Physics B: Atomic, Molecular and Optical Physics
J. Phys. B: At. Mol. Opt. Phys. **41** (2008) 225601 (4pp) doi:10.1088/0953-4075/41/22/225601

Direct observation of super-excited states in methane created by a femtosecond intense laser field

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Received 2 July 2008, in final form 15 October 2008
Published 7 November 2008

Abstract
We report, for the first time, a direct observation of the super-excited states of CH_4 in femtosecond intense laser fields using a pump (800 nm)–probe (1338 nm) technique. An unambiguous depletion of the CH ($A\,^2\Delta \rightarrow X\,^2\Pi$) fluorescence signal as a function of the delay time is attributed to the de-excitation of the super-excited states by the probe laser pulse. The lifetime of the super-excited state is measured to be about 160 fs.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The important features of super-excited states (SESs) of a molecule possessing an energy above the ionization potential were first proposed by Platzman in 1962 [1, 2]. SESs exist widely in radiation chemistry [1, 2], laser chemistry [3, 4], XUV photochemistry [5–7] and electron impact physics [8–10]. Much of recent work on SESs comes from using synchrotron radiation (SR) [11]. In this case, the VUV excitation pertains to only one SES at specific excitation energy. However, multi-photon excitation of a molecule caused by the intense femtosecond laser pulse creates more than one SES [12]. Since fs laser pulses can be controlled temporally, super excitation of a molecule by intense fs laser would, in principle, produce a new type of excitation complementary to the excitation by synchrotron radiation or other UV or XUV sources. Femtosecond laser excitation would be rich in physics and chemistry.

Currently, precise pathways and the final states in such super-excitation by fs lasers are still unknown because not much has been done in this direction yet. Recently, we proposed that the fluorescing CH fragments coming from the dissociation of CH_4 by an intense 45 fs Ti-sapphire laser pulse at around 800 nm could have been the result of super-excitation of some electronic states [3, 13]. Even though we do not know exactly what these states are, it is expected that such SESs which are coupled to the continuum should have a very short lifetime. In previous SR studies, the lifetime of SESs ($\tau = \hbar/\Gamma$) can only be determined indirectly by measuring the line width (Γ) of the SESs. In theory, several methods have been used to calculate the linewidth of SESs [14]. Indirect experimental estimate of SESs lifetime was provided through the linewidth of SESs by measuring the ratio of kinetic energy spectra of different isotopes of hydrogen atoms [15]. However, a simple and direct measurement of the SES's short lifetime is essential. This is done in the current work, using a pump-probe technique. We experimentally demonstrated for the first time that SESs of CH_4 excited by a fs Ti-sapphire laser indeed

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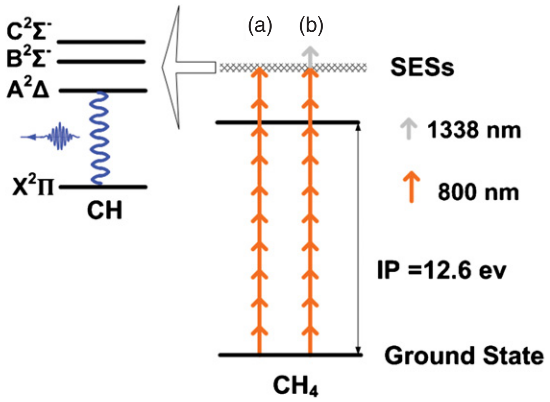

Figure 1. Schematic diagram of the SESs excitation of CH_4: (a) the process is just with the pump pulse to excite the SESs (the regions except for the dip in figure 4) and (b) the process of how the probe pulse depletes the SESs (the dip region in figure 4).

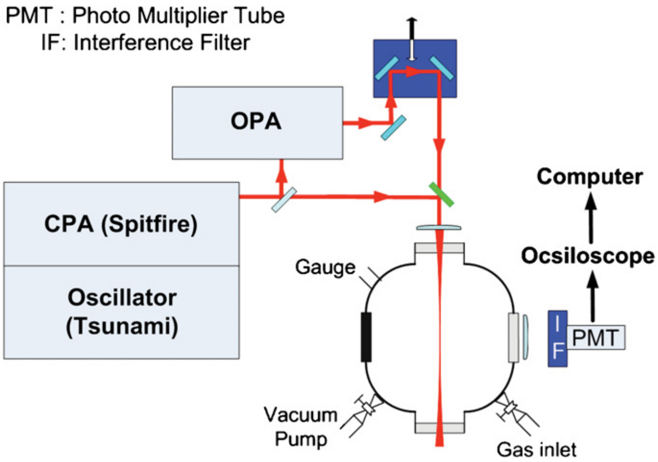

Figure 2. Sketch of the experimental setup.

have a very short lifetime of about 160 fs. This observation establishes unequivocally the existence of SESs and could open up a new direction in more complex molecular super excitation which could not be studied directly temporally using synchrotron radiation.

The main idea in this experiment is the following. We assume that the fs laser pulse excites the CH_4 into one of its SESs that decays quickly into the CH excited fragments which subsequently fluoresce. The various fluorescence spectra from the CH (A → X, B → X and C → X) bands as well as the hydrogen Balmer α-line have already been observed previously [3]. A delayed probe pulse at a different wavelength would destroy the SESs. Consequently, there will be a decrease in the CH fragments, hence a reduction in the CH fluorescence. This idea is shown schematically in figure 1. The excited state inside the ionization continuum is just a representation of the SES which is not yet precisely defined. The current experiment monitors only the strongest A → X band.

2. Experimental setup

The sketch of pump and probe experimental setup is illustrated in figure 2. A fs Ti-sapphire oscillator–regenerative amplifier system (Spectra Physics Tsunami/Spitfire) gives out 60 fs pulses at full width half maximum (FWHM) with a 1 kHz repetition rate, energy of 2 mJ per pulse and a diameter of about 5 mm ($1/e^2$ level of intensity). The pulses are slightly negatively chirped (the transform limited pulse duration is about 42 fs at FWHM). This negatively chirped pulse is optimized for the Optical Parametric Amplifier (OPA 800 C(tm) Spectra Physics) system. The laser beam was then separated into two arms by a 50/50 beam splitter. One was used as the pump beam (~900 μJ/pulse). The other was sent to an OPA to generate the infrared probe pulses at 1338 nm with a pulse duration of about 50 fs (FWHM) and pulse energy around 90 μJ. In the probe arm, a high-resolution delay line (40 nm) is used to collect the data versus the different delay times between the pump and probe pulses. The probe beam had a horizontal polarization parallel to that of the pump beam. Both of the laser beams were focused onto a vacuum chamber by a plano-convex lens ($f = 30$ cm). Spatial superposition of the two pulses was checked with a far-field measurement, while temporal superposition of these two pulses in air was checked by a four-wave mixing (4 WM) process, where two photons of 800 nm were mixed with one infrared photon ($2\omega_{800} - \omega_{\mathrm{ir}}$), leading to a yellowish laser emission [17]. This was used as a sign of the temporal superposition of these two pulses. Pure methane (CH_4 Praxair) was introduced to the chamber at an equilibrium pressure of 20 Torr with a background pressure of 4×10^{-2} Torr. The superposition of the two pulses was then fine tuned by observing a faint yellow light in the forward direction.

The fluorescence signal was imaged from the side onto a gated Micro Channel Plate Photo Multiplier Tube (MCP–PMT, Hamamatsu R5916 U-52) by a fused silica lens of $f = 10$ cm. A pulse generator (Hewlett Packard 8013B) was used to generate a delay gate signal for triggering the gated PMT. Moreover an interference filter which has a 2.5 nm (FWHM) in the transmission spectrum with the highest transmittance at 431 nm for the CH ($A\,^2\Delta \rightarrow X\,^2\Pi$) fluorescence was used to avoid unwanted photons. The output signal of the PMT was connected to an oscilloscope (Tektronix, TDS7254 2.5 GHz).

3. Results and discussion

In the recent work of Kato *et al* [16], the SESs of the methane molecules were studied by SR from 12.65 to 41 eV in which five SESs had been found and discussed. One of them is populated by the photon with the energy of around 14.5 eV resulting in CH (A) and CH (B) through neutral dissociation. It was noted that through this state excited hydrogen atoms cannot be generated because of the low energy of this state [16]. On the other hand, the excitation of methane with 800 nm fs laser pulses happens through absorbing 10 ± 1 photons (about 15 eV) [3, 13]. Although, in principle, fs laser excitation could be different from the VUV excitation, we observed the fluorescence emissions from CH (A, B, C → X) and H (Balmer α) [3]. This agrees with the CH (A, B → X)

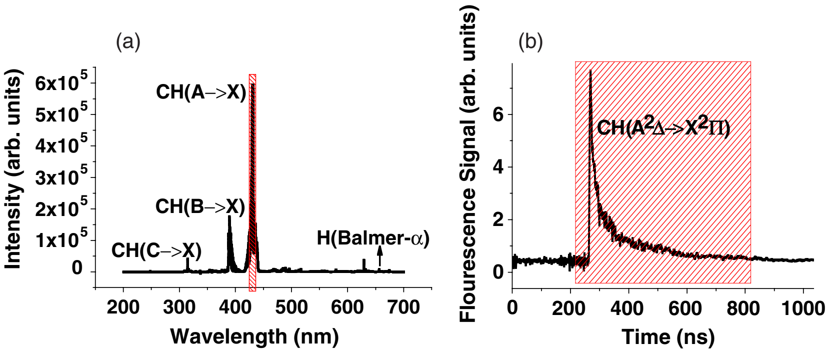

Figure 3. (a) A typical fluorescence spectrum of methane in the absence of the probe pulse. The rectangle shows the integration interval. (b) Typical fluorescence decay of CH ($A\,^2\Delta \rightarrow X\,^2\Pi$) with a 3 Torr pressure. The rectangle shows the integration period.

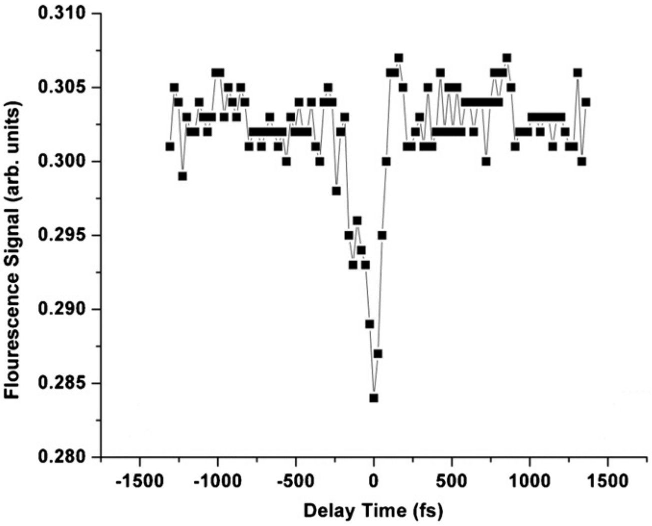

Figure 4. Integrated fluorescence signal of CH ($A\,^2\Delta \rightarrow X\,^2\Pi$) at around 431 nm versus the delay time between the pump and probe pulses; negative delay time means the probe pulses are behind the pump pulses.

results observed by the SR excitation and contains richer information. In the current experiment, the fluorescence signal of the CH ($A\,^2\Delta \rightarrow X\,^2\Pi$) band at 431 nm was measured as a function of the delay time between the pump and probe pulses. The data were averaged over 100 laser shots and the fluorescence signals were integrated within the wavelength range from 428.5 to 433.5 nm (see figure 3(a)), as well as within a time interval of 600 ns, in order to add up all the fluorescence in the temporal domain (see figure 3(b)). Figure 4 shows the fluorescence signal as a function of the delay time. It can clearly be seen that when the delay time between the pump and probe is around zero, an obvious decrease in the fluorescence signal takes place. The fluorescence decrease occurs within a dip width of about 160 fs (FWHM). Since the maximum correlation time of the pump and probe pulses is less than the dip's temporal width, we exclude the possibility of cross correlation of two pulses. It is noted that outside the dip the fluorescence signals keep almost constant; i.e. the probe pulse does no longer affect the dissociation. Our results clearly indicate that a dissociation channel of the CH excited fluorescing state has an intermediate state having the life time of about 160 fs that can be destroyed by the present probe pulse. Considering the effect of the pump and probe pulse durations on the dip shape, the lifetime would be in the range of 50–160 fs.

The decrease in the fluorescence signal is slightly more than 5% of the value obtained when the probe beam does not temporally overlap the pump pulse. This may mean that the SES can be destroyed only with a small probability by the present probe pulse, or there are other channels having intermediate states that are not destroyed by the present probe. If an SES has a small destroying probability, it would mean that the state is really imbedded inside the ionization continuum. This is because the probe pulse would not be able to efficiently couple a state inside the continuum (SES) to another state in the continuum such as ionization, etc. Further information on the SES could be given by future detailed experiment with probe pulses having various intensities and frequencies.

We emphasize that the fluorescence depletion could not be explained by a simple ionization scheme where the neutral CH products are generated by the disintegration of the CH_4^+ ion or generated by electron–ion recombination, since the lifetimes of these two processes are very long, in the nanosecond time scale. We would not have observed the depletion of the fluorescence only in a time zone of around 160 fs. Similarly, the fluorescence depletion does not refer to the direct interaction between the probe laser pulse and CH_2 or CH (A) species either, because the depletion takes place immediately after the first excitation without any time delay while the fluorescence lifetime of CH (A) is normally in the nanosecond time scale. A cascade dissociation mechanism of $CH_4 \rightarrow CH_2 \rightarrow CH$ is also excluded in [3].

4. Conclusion

In conclusion, by using a pump–probe method, we demonstrated direct evidence of SESs using, as an example, CH_4 in femtosecond intense laser fields. The decrease in the fluorescence signal of CH has been observed and attributed to the depletion of the SESs of CH_4. A new era is opened up to study SESs of molecules, especially their dynamics and characteristics induced by intense laser fields.

Acknowledgment

This work was partially supported by the NSERC, Canada Research Chairs, CIPI, DRDC-Valcartier and FQRNT. It was also supported by China Ministry of Science and Technology with the Project for Fundamental Research (2006CB806000). Technical support and assistants of Mr M Martin in the Ultrafast Intense Laser Science Lab at Université Laval, where the experiment was carried out is highly appreciated. AA and SLC would like to thank K Yamanouchi for his advice and fruitful discussion on the subject.

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