行政院國家科學委員會專題研究計畫 成果報告

強短脈衝雷射產生的超激發態的研究
研究成果報告(精簡版)

計 畫 類 別 ：個別型
計 畫 編 號 ：NSC 100-2113-M-009-006-
執 行 期 間 ：100 年 08 月 01 日至 101 年 07 月 31 日
執 行 單 位 ：國立交通大學應用化學系（所）

計 畫 主 持 人：寺西慶哲

計畫參與人員：碩士班研究生-兼任助理人員：彭冠瑋
碩士班研究生-兼任助理人員：胡智偉

公 開 資 訊 ：本計畫可公開查詢

中 華 民 國 101 年 10 月 24 日

中文摘要：當分子經由強雷射照射發光(波長在800nm情況下)，會導致各種非線性動力學的過程。例如分子的校準、結構改變離子化高階簡諧的產生或庫倫爆炸。然而，經由強雷射所導致的電子激發，比較不被重視。近年來，Kong 等人由強雷射照射各種氣體分子找到了電子激發態的中性碎片，且已知庫倫爆炸同時會導致各種化學鍵斷裂並產生帶電的碎片。即使 Kong 發現化學鍵斷裂的結果，也不會因為碎片是中性而歸因於庫倫爆炸，故這是一個新的機制。

我們假設碎片的產生是經由激發母體分子而來的，並且呈現寬廣的分佈。光子能量必須遠小於第一激發態，且大於或等於其他激發態之間的能量，就能呈現寬廣的分佈態。因為光子能量遠小於第一激發能，導致從基態到激發態的躍遷不易發生，而激發態之間的躍遷速度又比前者來的迅速。

無論最終態為何，都不會影響基態的躍遷趨勢，因為激發態之分布會重新且快速的平均分配至每個激發態(包含超激發態)上。其計算結果與近期實驗所發現的超激發態形成原因相符。

傳統的研究指出，可利用電子碰撞或同步輻射源來產生超激發態之現象，而強短脈衝亦具有開啟這方面研究的可能性，其原因為非線性激發過程能使強雷射製造出電子蹤撞或同步輻射源很難達成的超激發態，Kong 等人也發現某些氧氣分子確實具有超激發態之性質。另一因素為可利用時間析光譜儀來研究超激發態。Chin’s 研究團隊在 pump-probe 實驗中得知第一個脈衝能產生超激發態之現象，第二個脈衝則導致超激發態受到破壞，其結果能推測出超激發態的可能壽命。

在超激發態的研究中，雖然已經證明強短脈衝雷射是一個優良的方法，但仍有幾個基本問題依舊存在：為什麼超激發態可以存在於強雷射場中？母體分子在超激發態的碎片機制是什麼？pump-probe 實驗中，第二道脈衝又是如何破壞超激發態？故本篇研究重點著重於 (a)理論計算強短脈衝雷射到達超激發態或高階簡諧之過程 (b)超激發態的飛秒與阿秒動力學。

中文關鍵詞：強短脈衝雷射, 飛秒, 超激發態

英文摘要：When molecules are irradiated by an intense laser (which typical wavelength is about 800 nm), various nonlinear dynamical processes are induced. Examples are alignment, structural change, and ionization followed by high order harmonic generation or Coulomb explosion. Electronic excitation by an intense laser,

however, has been paid less attention.
Recently, Kong et al. found electronically excited neutral fragments after irradiating intense laser to various kind of gaseous molecule. It has been known that Coulomb explosion results in simultaneous breakings of various chemical bonds leading to charged fragments. Even though Kong's finding also results in breaking almost all the chemical bonds, it is not attributed to the Coulomb explosion, but to a new mechanism because the fragments are neutral. Conventional studies utilize electron scattering or synchrotron radiation to prepare SES's. intense short pulsed laser, on the other hand, may open new possibilities in this research field. Due to the non linearity of the pumping process, intense laser can produce SES's that can hardly be created by electron scattering or synchrotron radiation. Kong et al. actually found several new SES's of O2 molecule. Another consequence of intense short pulse laser is that time resolved spectroscopy is made possible. Chin's group performed a kind of pump-probe experiment, in which pump pulse creates SES's and probe pulse destroys them, obtaining a possible lifetime of SES.
Even though it is evident that intense short pulse laser is a new promising tool to study super excited states, several basic problems are still open as follows. Why can SES's survive in intense laser field? What is the fragmentation mechanism of parent molecule in SES? What is the mechanism to destroy SES in the pump probe experiment? The purpose of this research project is to give concrete answers to these problems. I am going to study on (a) pumping process to SES's and high harmonic generation by intense short pulse laser, and (b) femto- and atto- second dynamics of SES with/without laser irradiation.

英文關鍵詞： Intense Short Pulse, Femto Second, Super Excited State

附件一

行政院國家科學委員會補助專題研究計畫 ■成果報告 □期中進度報告

強短脈衝雷射產生的超激發態的研究

(Studies of Super Excited States Created by Intense Short Pulsed Laser)

計畫類別：☑個別型計畫　□整合型計畫
計畫編號：NSC 100 － 2113 － M － 009 － 006 －
執行期間： 100 年 08 月 01 日至 101 年 07 月 31 日

執行機構及系所：國立交通大學 物理所

計畫主持人：寺西慶哲
共同主持人：
計畫參與人員：彭冠瑋及胡智瑋

成果報告類型(依經費核定清單規定繳交)：☑精簡報告　□完整報告

本計畫除繳交成果報告外，另須繳交以下出國心得報告：
□赴國外出差或研習心得報告
□赴大陸地區出差或研習心得報告
□出席國際學術會議心得報告
□國際合作研究計畫國外研究報告

處理方式：除列管計畫及下列情形者外，得立即公開查詢
□涉及專利或其他智慧財產權，□一年□二年後可公開查詢

中　華　民　國　101　年　10　月　24　日

附件二

國科會補助專題研究計畫成果報告自評表

請就研究內容與原計畫相符程度、達成預期目標情況、研究成果之學術或應用價值（簡要敘述成果所代表之意義、價值、影響或進一步發展之可能性）、是否適合在學術期刊發表或申請專利、主要發現或其他有關價值等，作一綜合評估。

1. 請就研究內容與原計畫相符程度、達成預期目標情況作一綜合評估

☑ 達成目標

☐ 未達成目標（請說明，以 100 字為限）

☐ 實驗失敗

☐ 因故實驗中斷

☐ 其他原因

說明：無。

2. 研究成果在學術期刊發表或申請專利等情形：

論文：☑已發表 ☐未發表之文稿 ☐撰寫中 ☐無

(1) "Quantum Switching of pi-Electron Rotations in a Nonplanar Chiral Molecule by Using Linearly Polarized UV Laser Pulses", Mineo, Hirobumi; Yamaki, Masahiro; Teranishi, Yoshiyuki; Hayashi, Michitoshi; Lin, Sheng Hsien; Fujimura, Yuichi, Journal of the American Chemical Society, 134, PP.14279-PP.14282 (2012/08) SCI.

(2) "Thermodynamics of protein folding using a modified Wako-Saitô-Muñoz-Eaton model", Min-Yeh Tsai, Jian-Min Yuan, Yoshiaki Teranishi and Sheng Hsien Lin, Journal of Biological Physics, 38, PP.543-PP.571 (2012/09) SCI.

(3) "Neutral dissociation of hydrogen molecules in a strong laser field through superexcited states", A Azarm, D Song, K Liu, S Hosseini, Y Teranishi, S H Lin, A Xia, F Kong and S L Chin, Journal of Physics B: Atomic, Molecular and Optical Physics, 44, PP.085601 (2012/08) SCI.

(4) "A master equation approach to the dynamics of zero electron kinetic energy (ZEKE) states and ZEKE spectroscopy", Yi-Hsieh Wang, H. Mineo, S. D. Chao, H. L. Selzle, H. J. Neusser, E. W. Schlag, Y. Teranishi, and S. H. Lin, Journal of Chemical Physics, 134, PP.064316 (2011/02/11) SCI.

論文：☐已發表 ☐未發表之文稿 ☑撰寫中 ☐無

(5) "The enhancement of CH4 fluorescence in femtosecond intense laser fields", in preparation (2012) SCI.

(6) "Ionization/Dissociation Processes of Methyl-Substituted Derivates of Cyclopentanone in Intense Femtosecond Laser Field Corresponding", Alexander M. Mebel, Qiaoqiao Wang, Di Wu, Dongdong Zhang, Mingxing Jin, Fuchun Liu, Hang Liu, Zhang Hu, Dajun Ding, Yuri A Dyakov, Hirobumi Mineo, Yoshiaki Teranishi, Sheng Der Chao, Alexander M. Mebel and Sheng Hsien Lin, Chemical Physics, in preparation (2012) SCI.

論文：☐已發表☑未發表之文稿☐撰寫中 ☐無

(7) "Neutral fragmentation paths of methane induced by intense ultrashort pulses: Ab initio molecular orbital approach", *submitted to J. Phys. Chem. A* (2012) SCI.

專利：☐已獲得 ☐申請中☑無

技轉：☐已技轉 ☐洽談中☑無

其他：(以 100 字為限) 研討會論文

(1) "Highly Nonlinear Excitation of Molecule by Intense Laser Field", Yoshiaki Teranishi, **Invited talk**, at Mini-symposium on Ultrafast Intense Laser Science, at Laval University/ Canada, July 12-21 2012

(2) "Numerical Simulation of Quantum Control Spectroscopy for Overlapping Resonance with State Selectivity", Yoshiaki Teranishi, The 21th International Laser Physics Workshop (LPHYS12), **Invited talk**, at University of Calgary/ Canada, July 22-29, 2012

(3) "Laser control of atomic and molecular processes", 2012 years of theoretical computational chemistry workshop, Yoshiaki Teranishi, **Invited talk**, Institute of atomic and molecular sciences academia sinica, 浦大邦講堂, Feb. 24-25, 2012

3. 請依學術成就、技術創新、社會影響等方面，評估研究成果之學術或應用價值（簡要敘述成果所代表之意義、價值、影響或進一步發展之可能性）（以 500 字為限）

When molecules are irradiated by an intense laser (which typical wavelength is about 800 nm), various nonlinear dynamical processes are induced. Examples are alignment, structural change, and ionization followed by high order harmonic generation or Coulomb explosion. Electronic excitation by an intense laser, however, has been paid less attention.

Recently, Kong et al. found electronically excited neutral fragments after irradiating intense laser to various kind of gaseous molecule. It has been known that Coulomb explosion results in simultaneous breakings of various chemical bonds leading to charged fragments. Even though Kong's finding also results in breaking almost all the chemical bonds, it is not attributed to the Coulomb explosion, but to a new mechanism because the fragments are neutral.

We have proposed a theoretical model that explains this new phenomenon. We assume that fragmentation occurs from excited parent molecule created by a new excitation mechanism having a wide distribution of the final states. We assume that the first excitation energy is much larger than the photon energy, and that energy spacing between excited states are as same as or smaller than the photon energy. Accordingly the excitation hardly takes place from the ground state because of the large excitation energy, whereas the transitions between excited states are much faster than the transition from the ground state. Excitation probabilities from the ground state consequently do not depend on the final state because the population of an excited state tends to be redistributed rapidly among excited states. Our model indicates that even super excited states (SES's) are created, which was confirmed by recent experiments.

In this project we theoretically discuss the excitation of molecule by intense laser pulse. We have found (1) parity dependence of the excitation probabilities in the excitation of Hydrogen atom, (2) enhancement of excitation probability by an additional weak 400nm pulse, (3) and dissociation mechanism of methane in intense laser fields. (1) leads to the detail mechanism of the excitation and an explanation of the stability of SES's in intense laser fields. The enhancement mechanism in (2) is expected to be applied to high harmonic generation, which may open a new possibility to generate intense X-ray lasers. (3) is the first attempt to explain the neutral fragmentation after electronic excitation. We have determined the two channels which results in neutral dissociation and ionic dissociation, respectively.

研究成果如下所示：

依序為封面、目錄（精簡報告得省略）、中英文摘要及關鍵詞、報告內容、參考文獻、計畫成果自評、可供推廣之研發成果資料表、附錄。

(一)報告封面：請至本會網站（http：//www.nsc.gov.tw）線上製作（格式如附件一）。
(二)中、英文摘要及關鍵詞 (keywords)。

中文關鍵詞：

強短脈衝雷射, 飛秒, 超激發態

中文摘要：

當分子經由強雷射照射發光(波長在 800nm 情況下)，會導致各種非線性動力學的過程。例如分子的校準、結構改變離子化高階簡諧的產生或庫倫爆炸。然而，經由強雷射所導致的電子激發，比較不被重視。近年來，Kong 等人由強雷射照射各種氣體分子找到了電子激發態的中性碎片，且已知庫倫爆炸同時會導致各種化學鍵斷裂並產生帶電的碎片。即使 Kong 發現化學鍵斷裂的結果，也不會因為碎片是中性而歸因於庫倫爆炸，故這是一個新的機制。

我們假設碎片的產生是經由激發母體分子而來的，並且呈現寬廣的分佈。光子能量必須遠小於第一激發態，且大於或等於其他激發態之間的能量，就能呈現寬廣的分佈態。因為光子能量遠小於第一激發能，導致從基態到激發態的躍遷不易發生，而激發態之間的躍遷速度又比前者來的迅速。

無論最終態為何，都不會影響基態的躍遷趨勢，因為激發態之分布會重新且快速的平均分配至每個激發態(包含超激發態)上。其計算結果與近期實驗所發現的超激發態形成原因相符。

傳統的研究指出，可利用電子碰撞或同步輻射源來產生超激發態之現象，而強短

脈衝亦具有開啟這方面研究的可能性，其原因為非線性激發過程能使強雷射製造出電子踫撞或同步輻射源很難達成的超激發態，Kong 等人也發現某些氧氣分子確實具有超激發態之性質。另一因素為可利用時間析光譜儀來研究超激發態。Chin's 研究團隊在 pump-probe 實驗中得知第一個脈衝能產生超激發態之現象，第二個脈衝則導致超激發態受到破壞，其結果能推測出超激發態的可能壽命。

在超激發態的研究中，雖然已經證明強短脈衝雷射是一個優良的方法，但仍有幾個基本問題依舊存在：為什麼超激發態可以存在於強雷射場中？母體分子在超激發態的碎片機制是什麼？pump-probe 實驗中，第二道脈衝又是如何破壞超激發態？故本篇研究重點著重於 (a)理論計算強短脈衝雷射到達超激發態或高階簡諧之過程 (b)超激發態的飛秒與阿秒動力學。

English Keywords：

Intense Short Pulse, Femto Second, Super Excited State

English Abstract：

When molecules are irradiated by an intense laser (which typical wavelength is about 800 nm), various nonlinear dynamical processes are induced. Examples are alignment, structural change, and ionization followed by high order harmonic generation or Coulomb explosion. Electronic excitation by an intense laser, however, has been paid less attention.

Recently, Kong et al. found electronically excited neutral fragments after irradiating intense laser to various kind of gaseous molecule. It has been known that Coulomb explosion results in simultaneous breakings of various chemical bonds leading to charged fragments. Even though Kong's finding also results in breaking almost all the chemical bonds, it is not attributed to the Coulomb explosion, but to a new mechanism because the fragments are neutral.

We have proposed a theoretical model that explains this new phenomenon. We assume that fragmentation occurs from excited parent molecule created by a new excitation mechanism having a wide distribution of the final states. We assume that the first excitation energy is much larger than the photon energy, and that energy spacing between excited states are as same as or smaller than the photon energy. Accordingly the excitation hardly takes place from the ground state because of the large excitation energy, whereas the transitions between excited states are much faster than the transition from the ground state. Excitation probabilities from the ground state consequently do not depend on the final state because the population of an excited state tends to be redistributed rapidly among excited states. Our model indicates that even super excited states (SES's) are created, which was confirmed by recent experiments.

Conventional studies utilize electron scattering or synchrotron radiation to prepare SES's. intense short pulsed laser, on the other hand, may open new possibilities in this research field. Due to the non linearity of the pumping process, intense laser can produce SES's that can hardly be created by electron scattering or synchrotron radiation. Kong et al. actually found several new SES's of O2 molecule. Another consequence of intense short pulse laser is that time resolved spectroscopy is made possible. Chin's group performed a kind of

pump-probe experiment, in which pump pulse creates SES's and probe pulse destroys them, obtaining a possible lifetime of SES.

Even though it is evident that intense short pulse laser is a new promising tool to study super excited states, several basic problems are still open as follows. Why can SES's survive in intense laser field? What is the fragmentation mechanism of parent molecule in SES? What is the mechanism to destroy SES in the pump probe experiment? The purpose of this research project is to give concrete answers to these problems. I am going to study on (a) pumping process to SES's and high harmonic generation by intense short pulse laser, and (b) femto- and atto- second dynamics of SES with/without laser irradiation.

(三)報告內容：包括前言、研究目的、文獻探討、研究方法、結果與討論（含結論與建議）...等。

Introduction

The inventions of mode-locked oscillators and chirped pulse amplifiers have opened a new possibility of intense field science. Peta-watt peak intensity is now available by tabletop lasers, and numerous new phenomenon and technologies have been revealed so far. When molecules are irradiated by an intense laser, various nonlinear dynamical processes are induced. Examples are alignment, structural change, and ionization followed by high order harmonic generation or Coulomb explosion. Electronic excitation by an intense laser, however, has been paid less attention.

Recently, Kong et al. (in the collaboration with S. L. Chin's group of Laval Univ.) found electronically excited neutral fragments after irradiating intense laser to various kinds of gaseous molecule such as methane, ethylene, and n-butane. It has been known that Coulomb explosion results in simultaneous breakings of various chemical bonds leading to charged fragments. Even though Kong's finding also results in breaking almost all the chemical bonds, it is not attributed to the Coulomb explosion, but to a new mechanism because the fragments are neutral.

We have proposed a theoretical model that explains this new phenomenon[1]. We assume that fragmentation occurs from excited parent molecules created by a new excitation mechanism, which has a wide distribution of the final state in the excited states. In our model we assume that the first excitation energy is much larger than the photon energy, and that energy spacing between excited states are as same as or smaller than the photon energy. Accordingly the excitation hardly takes place from the ground state because of the large excitation energy, whereas the transitions between excited states are much faster than the transition from the ground state. Excitation probabilities from the ground state consequently do not depend on the final state because population of an excited state tends to be redistributed rapidly among excited states due to the small energy separations. In the case of methane the excitation probabilities to almost all the excited states have power dependence on the laser intensity, namely I^{10}, which corresponds to the experimental observation of laser intensity dependence of the fluorescence of CH fragment in the A state having the power dependence of I^{10}. Our model indicates that even super excited states (SES's) are created, which also agrees well with the experimental results.

Conventional studies utilize electron scattering or synchrotron radiation to prepare SESs. Intense short pulsed laser, on the other hand, may open new possibilities in this research field. Due to the non linearity of the pumping process, intense laser can produce SESs that can hardly be created by electron scattering or synchrotron radiation. Kong et al. actually found several new SESs of O2 molecule[3]. Another consequence of intense short

pulse laser is that time resolved spectroscopy is made possible. Ali et al. (S. L. Chin's group) performed a kind of pump-probe experiment[4], in which pump pulse creates SES's and probe pulse destroys them, obtaining a possible life time of SES.

Purpose

Even though it is evident that intense short pulse laser is a new promising tool to study super excited states, several basic problems are still open as follows. Why can SESs survive in intense laser field? What is the fragmentation mechanism of parent molecule in SES? What is the mechanism to destroy SES in the pump probe experiment by Ali et al.? The purpose of this research project is to give concrete answers to these problems. I am going to study on (a) pumping process to SESs and high harmonic generation by intense short pulse laser, (b) effect of second probe pulse, and (c) Dissociation process of methane in intense laser field.

Reference

[1] F. Kong, Q. Luo, H. Xu, M. Sharifi, D. Song, and S. L. Chin, J. Chem. Phys. **125**, 13320 (2006).

[2] Y. Teranishi, M. Hayashi, F Kong, S. L. Chin, S. D. Chao, H. Mineo, and S. H. Lin, "Highly multiphoton molecular excitation by an intense laser pulse", Mol. Phys. **106**, 333 (2008). (Prof. R. D. Levine's special issue).

[3] D. Song, A. Azarm, Y Kamali, K. Liu, A. Xia, Y. Teranishi, S. H. Lin, F. Kong, S. L. Chin,"Neutral dissociation of superexcited oxygen molecules in intense laser fields", J. Chem. Phys. **A 114**, 3087 (2010).

[4] A. Azarm, H. L. Xu , Y. Kamali, J. Bernhardt, D. Song, A. Xia, Y. Teranishi, S. H. Lin, F. Kong, S. L. Chin, "Direct observation of super-excited states in methane created by a femtosecond intense laser field", J. Phys. **B41**, 225601 (2008).

[5] A. Azarm, S. Ramakrishna, A. Talebpour, S. Hosseini, Y. Teranishi, H. L. Xu, Y. Kamali, J. Bernhardt, S. H. Lin, T. Sideman, and S. L. Chin, "Population Trapping and Rotational Revival of N2 Molecules During Filamentation of a Femtosecond Laser Pulse in Air", J. Phys. **B43**, 235602 (2010).

Methods

In this study, we consider the dynamics of molecular electronic states under an intense laser field. By taking the dipole approximation and ignoring the rovibrational motion, the total Hamiltonian of the system is given by

$$H(t) = H_0 + V(t). \tag{1}$$

Here, H_0 is the time-independent molecular Hamiltonian, and $V(t)$ is the time dependant interaction. In the dipole approximation, we have $V(t) = xF(t)\sin(\omega t)$.

We assume that our target molecule is described by a wavefunction $\Psi(t)$ satisfying the initial condition $\Psi(t=-\infty) = \Phi_i$. Here Φ_i is the *i*th eigenfunction of the molecular Hamiltonian $H_0(r)$, namely

$$H_0(r)\Phi_i = E_i\Phi_i. \tag{2}$$

where E_i is the eigen energy of the *i*th eigen function Φ_i. The excitation probability to the *j*th excited state P_{ij} is defined by

$$P_{ij} = \left|\left\langle \Phi_j \middle| \Psi(t=\infty)\right\rangle\right|^2, \tag{3}$$

where $\Psi(t=\infty)$ is obtained by solving the Schrodinger equation given by

$$i\frac{d}{dt}\Psi(t) = H(t)\Psi(t) \tag{4}$$

This equation is solved either by the direct numerical method or the Fourier-Floquet expansion method. In our formulation, the time dependent wavefunction $\Psi(t)$ is expanded by time independent basis functions, namely,

$$\Psi(t) = \sum_j c(t)\psi_j, \tag{5}$$

where $c(t)$ is the time dependent expansion coefficient, and ψ_j is the basis function. We have utilized bound state wavefunctions for the basis functions. In order to discuss the effect of continuum states, we utilize the Sturmian basis function, which satisfies the potential weighted Schrodinger equation,

$$\left[-\frac{1}{2}\Delta - \zeta_j\tilde{V}(r) - \varepsilon\right]\psi_j = 0. \tag{6}$$

Here $\tilde{V}(r) \equiv \frac{1}{r}$ is the Coulomb potential. It should be noted that ε is not an eigenvalue of eq.(6), but an arbitrary given parameter to determine the nature of the basis set. Eivenvalue problem (6) is solved for a given ε to obtain the eigenvalue ζ_j and the associated eigenfunction ψ_j. Since ζ_j may be interpreted as the electric charge of nucleus, our basis set consists of Coulombic wavefunctions with various different nuclear charges. It should

be noted that the eigenfunctions ψ_j do not satisfy the orthonormality relations, namely

$$\langle \psi_j | \psi_i \rangle \equiv S_{ij} \neq \delta_{ij}, \tag{7}$$

but satisfy the potential weighted orthonormality relation given by,

$$\langle \psi_j | V(r) | \psi_i \rangle = \delta_{ij}. \tag{8}$$

It is proven that the Sturmian basis set is a complete set, which can describe not only the bound states but also the continuum states. Substituting eq.(4) into the time dependent Schrodinger equation, we obtain

$$i\frac{d}{dt}c_{j'}(t) = \sum_j \left[H_{j'j} + S_{j'j} \right] c_j(t), \tag{9}$$

where $H_{j'j}$ is the Hamiltonian matrix element given by

$$H_{j'j}(t) = \langle \psi_{j'} | H(t) | \psi_j \rangle. \tag{10}$$

Results and Discussion

Effect of continuum and parity dependence of the slope

In this project, we first discuss the dynamics of a hydrogen atom induced by intense femto-second laser field. By utilizing the Sturmian basis function, we can discuss the ionization probabilities and effect of continuum states in the excitation probabilities. Fig.1 shows the total ionization and the total excitation probabilities of Hydrogen as the functions of laser intensity ($10^{-8} \sim 10^{-14}$ W/cm^2). Here "total" means that the ionization/excitation probabilities are summed up over the final states. Both the total ionization and the total excitation probabilities show power dependences with the power 9 and 10, respectively, which tendency agrees with ionization probabilities obtained by KFR theory and with excitation probabilities obtained by ignoring the continuum states.

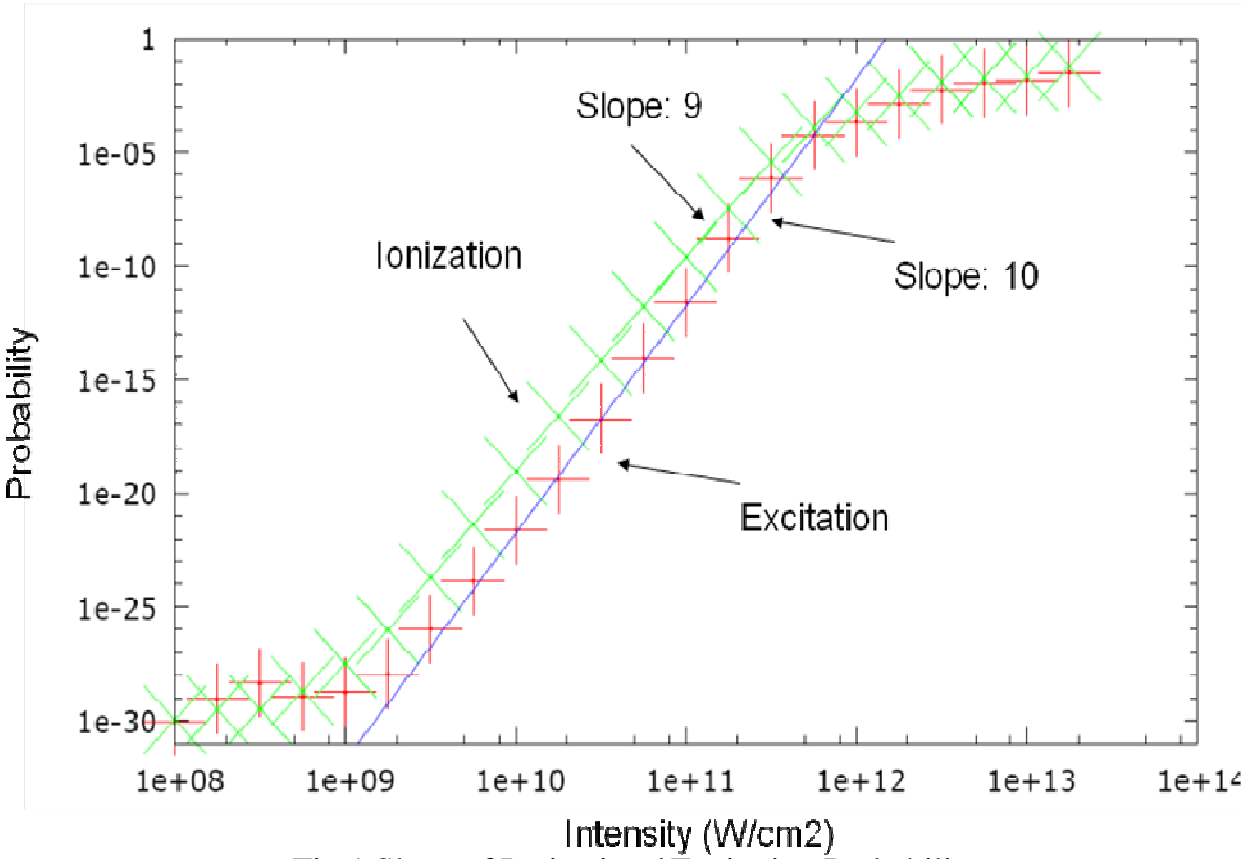

Fig.1 Slope of Ionization / Excitation Probability

If we plot the state specified excitation probability (, which is the excitation probability into each excited state) as function of laser intensity, we found two powers (namely, 9 or 10) depending on the final states. The state dependence of the power is summarized in Table.1. As is seen from the table, odd (even) angular momentum states

have slope of 10 (9). This parity dependence of the power implies the mechanism of intense field excitation as follows: Since the highly excited states are energetically closely lying, rapid Raman type transitions between highly excited states are induced by intense lasers. We have found that ionization shows the same parity dependence as well. Thus we concluded that continuum and bound states are also strongly coupled by Raman transition, and this is the reason why SES are stable under intense laser field. We are now analyzing this parity dependence and Raman transition by using the Floquet theory in order to discuss the details.

Angular Momentum Quantum Number *l*

Principle Quantum Number *n* \ *l*	0	1	2	3	4	5	6	7	8	9
1	*	-	-	-	-	-	-	-	-	-
2	10	9	-	-	-	-	-	-	-	-
3	9	10	9	-	-	-	-	-	-	-
4	9	10	9	10	-	-	-	-	-	-
5	10	9	10	9	10	-	-	-	-	-
6	10	9	10	9	10	9	-	-	-	-
7	10	9	10	9	10	9	10	-	-	-
8	10	9	10	9	10	9	10	9	-	-
9	10	9	10	9	10	9	10	9	10	-
10	10	9	10	9	10	9	10	9	10	9

Table1. Slope of Excitation Probability

Strong enhancement of excitation probability by double pulse scheme

Recently Chin's group performed new pump-probe type experiment with intense 800nm pulse and weak 400nm pulse. Their results are summarized in Fig.2. They observed the enhancement of fluorescence signal when two laser pulses overlap. One interesting feature in this result may be that there is no fluorescence signal if only 400nm pulse is applied, but the 400nm pulse enhances the fluorescence significantly if it is

irradiated together with the 800nm pulse.

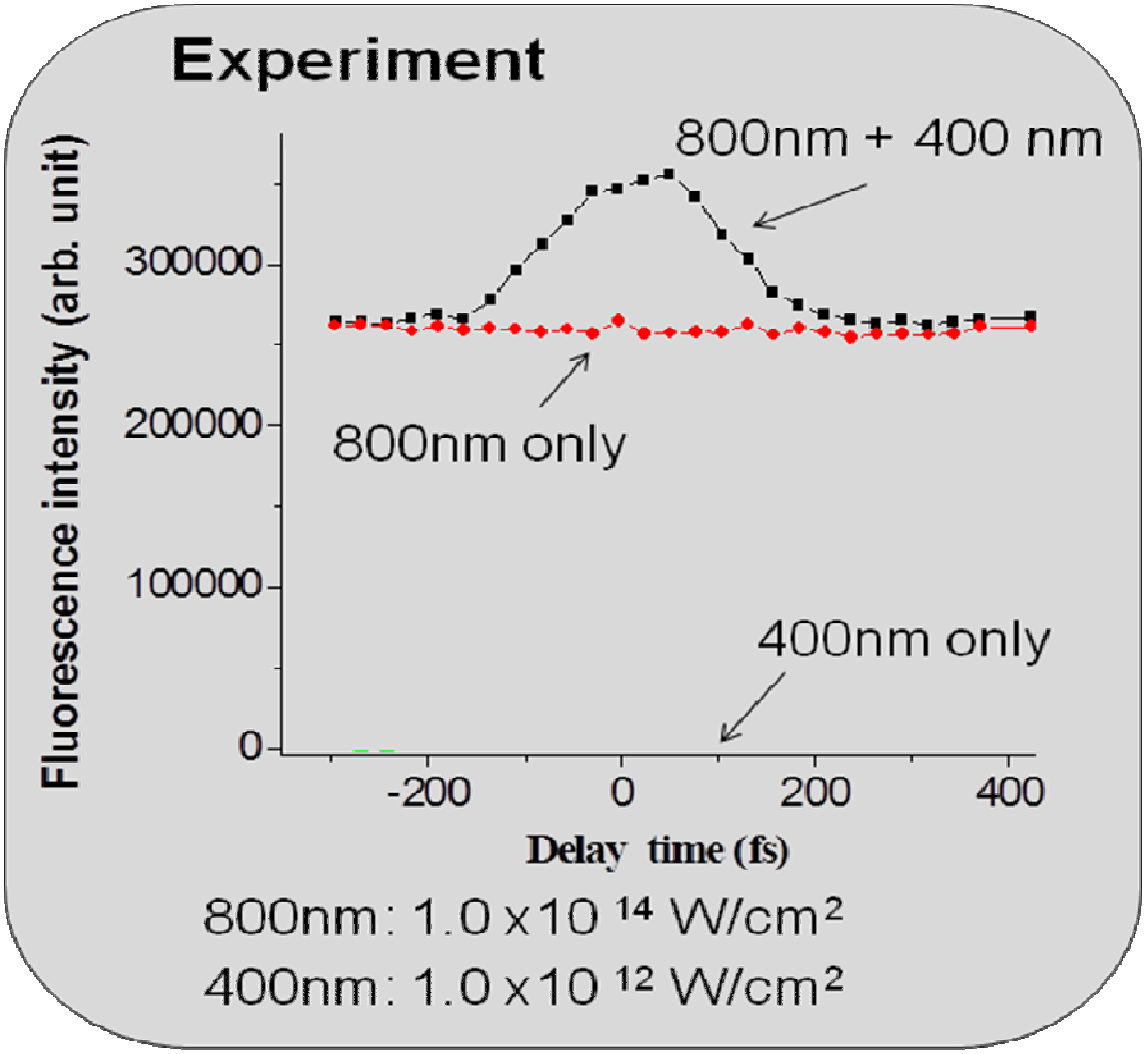

Fig.2 Experimental Results by Xu et. Al.

We have made a numerical simulation on this enhancement process with using only bound basis functions. The results are shown in Fig.3. As we see from Fig.3, a similar enhancement is reproduced by our simulation. In order to analyze the mechanism of this enhancement, we made a series of simulations with various intensities of 400nm pulse. The results are shown in Fig.4. In the low energy region ($I \le 10^9$ W/cm^2) the enhancement is proportional to the intensity, while in the higher energy region ($I > 10^{10}$ W/cm^2), it is proportional to I^2. From these numerical results, we proposed the mechanism of the enhancement as follows: By the 800 nm pulse highly excited states are strongly coupled forming Floquet states. In the case of only 800nm pulse irradiated, the transition from the ground state to the Floquet state is also induced by the absorption of the same 800nm photon. Since the 400nm pulse is not so intense to create Floquet states, the additional

400nm pulse can only induce the transition from the ground state to the Floquet states created by the intense 800nm pulse. This is the reason why the power dependence shown in Fig. 4 is linear of quadratic. We are now writing the manuscript on this enhancement phenomenon for publication.

This enhancement mechanism can also be applied to high harmonic generation processes. Now I am carrying out numerical simulations to prove it.

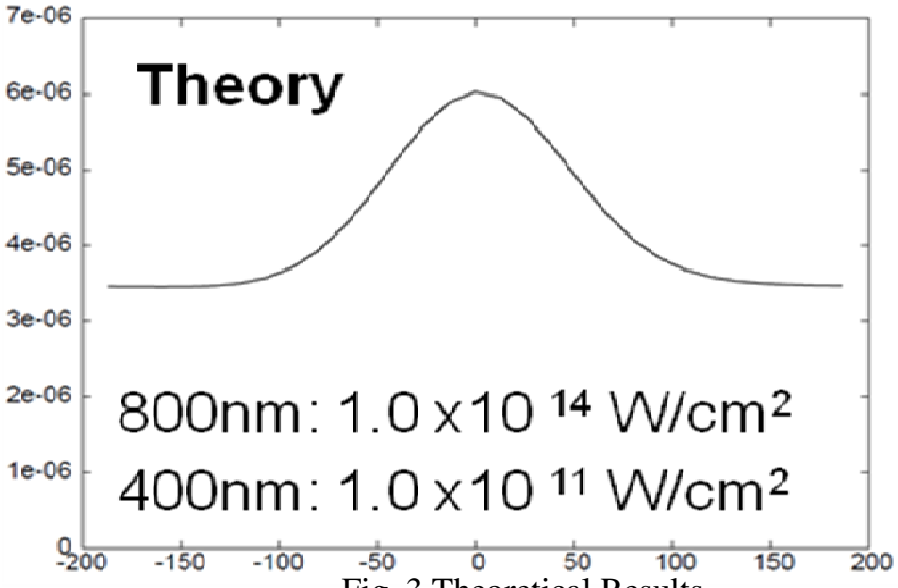

Fig. 3 Theoretical Results

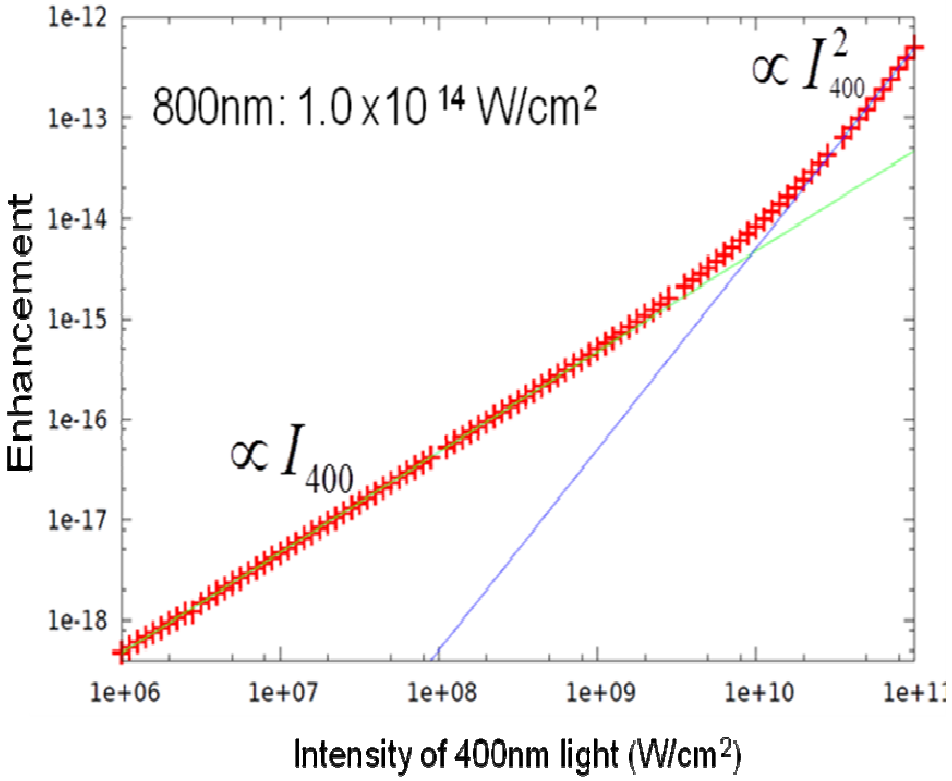

Fig. 4 Intensity dependence of enhancement

Dissociation of methane in electronically excited states in intense laser fields.

So far, we have discussed only the excitation processes of molecule. They observe in experiments, however, the fluorescence from fragments, and we have to discuss the dissociation process to fully explain the experimental results. For this purpose, we calculated instantaneous (laser field-dependent) potential energy curves leading to neutral fragmentations of methane at several points of laser intensities of 1.4×10^{13} to 1.2×10^{14} W/cm^2 (1.0×10^{10} to 3.0×10^{10} V/m) by using *ab initio* molecular orbital (MO) methods. Two fragmentation paths, CH_2 + 2H and $CH_2 + H_2$, in $^1T_2$ SES that are located in energy ranges of 12~16 eV were considered as the reaction paths since these states are responsible for Jahn-Teller to open up reaction paths during ultrashort pulses. As field intensity increased, the low-lying excited $^1A_1$ states originated from the Jahn-Teller $^1T_2$ states were substantially stabilized along the neutral fragment path along the dissociation $CH_4 \rightarrow CH_2 + 2H$ and were located below the ionization threshold. On the other hand, the low-lying excited $^1B_1$ states, which are also originated from the Jahn-Teller $^1T_2$ states, were embedded on the ionized state along the dissociation path to $CH_2 + H_2$. This indicates that ionic fragments, rather than neutral ones, are produced along the $CH_2 + H_2$ path. The different laser intensity dependence between the two paths can be explained in terms of the polarizability dependence: the polarizability along the $CH_4 \rightarrow CH_2 + 2H$ path increases, which brings about the stabilization, while the polarizability along the $CH_2 + H_2$ path does not. The computational results support neutral fragmentations via superexcited states proposed by Kong *et al.*. We have submitted a paper on this to Journal of Physical Chemistry A.

國科會補助計畫衍生研發成果推廣資料表

日期:2012/08/29

國科會補助計畫	計畫名稱: 強短脈衝雷射產生的超激發態的研究
	計畫主持人: 寺西慶哲
	計畫編號: 100-2113-M-009-006- 學門領域: 理論與計算化學

無研發成果推廣資料

100 年度專題研究計畫研究成果彙整表

計畫主持人：寺西慶哲	**計畫編號：**100-2113-M-009-006-
計畫名稱：強短脈衝雷射產生的超激發態的研究	

成果項目			量化			單位	備註（質化說明：如數個計畫共同成果、成果列為該期刊之封面故事...等）
			實際已達成數（被接受或已發表）	預期總達成數(含實際已達成數)	本計畫實際貢獻百分比		
國內	論文著作	期刊論文	0	0	100%	篇	
		研究報告/技術報告	0	0	100%		
		研討會論文	0	0	100%		
		專書	0	0	100%		
	專利	申請中件數	0	0	100%	件	
		已獲得件數	0	0	100%		
	技術移轉	件數	0	0	100%	件	
		權利金	0	0	100%	千元	
	參與計畫人力（本國籍）	碩士生	0	0	100%	人次	
		博士生	0	0	100%		
		博士後研究員	0	0	100%		
		專任助理	0	0	100%		
國外	論文著作	期刊論文	4	7	100%	篇	1. Quantum Switching of pi-Electron Rotations in a Nonplanar Chiral Molecule by Using Linearly Polarized UV Laser Pulses, Mineo, Hirobumi ; Yamaki, Masahiro ; Teranishi, Yoshiyuki ; Hayashi, Michitoshi ; Lin, Sheng Hsien ; Fujimura, Yuichi, Journal of the American Chemical Society, 134, PP.14279-PP.14282 (2012/08) SCI

							Hsien Lin, Journal of Biological Physics, 38, PP.543-PP.571 (2012/09) SCI. 3. Neutral dissociation of hydrogen molecules in a strong laser field through superexcited states, A Azarm, D Song, K Liu, S Hosseini, Y Teranishi, S H Lin, A Xia, F Kong and S L Chin, Journal of Physics B: Atomic, Molecular and Optical Physics, 44, PP.085601 (2012/08) SCI. 4. A master equation approach to the dynamics of zero electron kinetic energy (ZEKE) states and ZEKE spectroscopy, Yi-Hsieh Wang, H. Mineo, S. D. Chao, H. L. Selzle, H. J. Neusser, E. W. Schlag, Y. Teranishi, and S. H. Lin, Journal of Chemical Physics, 134, PP.064316 (2011/02/11) SCI. 5. The enhancement of CH4 fluorescence in femtosecond intense laser fields, in preparation (2012) SCI. 6. Ionization/Dissociation Processes of Methyl-Substituted Derivates of Cyclopentanone in Intense Femtosecond Laser Field Corresponding, Alexander M. Mebel, Qiaoqiao Wang, Di Wu, Dongdong Zhang, Mingxing Jin, Fuchun Liu, Hang Liu, Zhang Hu, Dajun

							Ding, Yuri A Dyakov, Hirobumi Mineo, Yoshiaki Teranishi, Sheng Der Chao, Alexander M. Mebel and Sheng Hsien Lin, Chemical Physics, in preparation (2012) SCI. 7. Neutral fragmentation paths of methane induced by intense ultrashort pulses: Ab initio molecular orbital approach, submitted to J. Phys. Chem. A (2012) SCI.
		研究報告/技術報告	0	0	100%		
		研討會論文	3	3	100%		1. Highly Nonlinear Excitation of Molecule by Intense Laser Field, Yoshiaki Teranishi, Invited talk, at Mini-symposium on Ultrafast Intense Laser Science, at Laval University/ Canada, July 12-21 2012 2. Numerical Simulation of Quantum Control Spectroscopy for Overlapping Resonance with State Selectivity, Yoshiaki Teranishi, The 21th International Laser Physics Workshop (LPHYS12), Invited talk,

							講堂, Feb. 24-25, 2012
		專書	0	0	100%	章/本	
	專利	申請中件數	0	0	100%	件	
		已獲得件數	0	0	100%		
	技術移轉	件數	0	0	100%	件	
		權利金	0	0	100%	千元	
	參與計畫人力（外國籍）	碩士生	3	3	100%	人次	彭冠瑋及胡智瑋
		博士生	0	0	100%		
		博士後研究員	0	0	100%		
		專任助理	0	0	100%		
其他成果 (無法以量化表達之成果如辦理學術活動、獲得獎項、重要國際合作、研究成果國際影響力及其他協助產業技術發展之具體效益事項等，請以文字敘述填列。)		無。					

	成果項目	量化	名稱或內容性質簡述
科教處計畫加填項目	測驗工具(含質性與量性)	0	
	課程/模組	0	
	電腦及網路系統或工具	0	
	教材	0	
	舉辦之活動/競賽	0	
	研討會/工作坊	0	
	電子報、網站	0	
	計畫成果推廣之參與（閱聽）人數	0	

國科會補助專題研究計畫成果報告自評表

請就研究內容與原計畫相符程度、達成預期目標情況、研究成果之學術或應用價值（簡要敘述成果所代表之意義、價值、影響或進一步發展之可能性）、是否適合在學術期刊發表或申請專利、主要發現或其他有關價值等，作一綜合評估。

1. 請就研究內容與原計畫相符程度、達成預期目標情況作一綜合評估 ■達成目標 □未達成目標（請說明，以 100 字為限） □實驗失敗 □因故實驗中斷 □其他原因 說明：
2. 研究成果在學術期刊發表或申請專利等情形： 論文：□已發表 □未發表之文稿 ■撰寫中 □無 專利：□已獲得 □申請中 ■無 技轉：□已技轉 □洽談中 ■無 其他：(以 100 字為限)
3. 請依學術成就、技術創新、社會影響等方面，評估研究成果之學術或應用價值（簡要敘述成果所代表之意義、價值、影響或進一步發展之可能性）(以 500 字為限)