

行政院國家科學委員會專題研究計畫 成果報告

一：飛秒超強光雷射化學之研究；二：有機太陽能電池光
物理之研究

研究成果報告(精簡版)

計畫類別：個別型

計畫編號：NSC 97-2113-M-009-011-

執行期間：97年08月01日至98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：林聖賢

處理方式：本計畫可公開查詢

中 華 民 國 98 年 10 月 29 日

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

一：飛秒超強光雷射化學之研究；二：有機太陽能電池光物理之研究

計畫類別：☒ 個別型計畫 ☐ 整合型計畫

計畫編號：NSC 97 - 2113 - M - 009 - 011 -

執行期間：2008 年 08 月 01 日至 2009 年 07 月 31 日

計畫主持人：林聖賢

共同主持人：

計畫參與人員：博士後研究-許瑛珍、方安磊、八卷昌弘、莫燕；研究助理(碩士級)-林思德；博士班研究生-蔡旻燁、蔡沛昌；碩士班研究生-朱冠宇

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

本成果報告包括以下應繳交之附件：

- ☐ 赴國外出差或研習心得報告一份
- ☐ 赴大陸地區出差或研習心得報告一份
- ☐ 出席國際學術會議心得報告及發表之論文各一份
- ☐ 國際合作研究計畫國外研究報告書一份

處理方式：除產學合作研究計畫、提升產業技術及人才培育研究計畫、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

執行單位：國立交通大學應用化學系(所)

中 華 民 國 98 年 10 月 26 日

〔 中文摘要 〕

關鍵字：高功率雷射、游離—解離、超激發、吸收與螢光光譜、內轉換、圓錐交點、非簡諧效應

本計畫包含兩部分。第一部分為飛秒高功率雷射化學研究，今年我們的焦點在於與實驗團隊（吉林大學 D. Ding 教授、Laval University 的 S. L. Chin 教授）合作，研究多原子分子之高功率雷射游離／解離，以及高功率雷射所致原子與分子超激發，已發表五篇論文，主要目的之一是探究利用飛秒高功率雷射作為新一代質譜技術的可行性。

第二部分為有機發光二極體、有機太陽能電池吸收與放射光譜和光物理過程之理論研究，已發表八篇論文。由分子非簡諧性位能面之全從始計算的可行性著手，我們已研究了非簡諧性對於分子紫外光—可見光吸收與放射光譜、非放射性躍遷及光致電子轉移的影響，圓錐交點對於分子光譜和無輻射過程的影響亦有探究。

〔 Abstract 〕

Keywords：high-power laser、ionization-dissociation、super-excitation、absorption and fluorescence spectra、internal conversion、conical intersection、anharmonic effect

This project consists of two parts. Part I is concerned with the investigations of femtosecond high-power laser chemistry. Our focus this year is to collaborate with the experimental groups (Prof. D. Ding of Jilin University and Prof. S. L. Chin of Laval University) to study the high-power laser ionization/dissociation of polyatomic molecules, and high-power laser induced super-excitation of atoms and molecules. Five papers have been published. One of the main purposes is to examine the possibility of employing a fs high-power laser to develop a new type of mass spectrometry.

Part II is concerned with the theoretical investigations of absorption and emission spectroscopies and photophysical processes in OLED and organic solar cells. Eight papers have been published. In view of the possibility of ab initio calculation of anharmonic potential surfaces of molecules, we have studied the anharmonic effect on UV-visible absorption and emission spectra of molecules, radiationless transitions and photo-induced electron transfer. Effect of conical intersection on molecular spectroscopies and internal conversion has also been studied.

Part I Investigations of Femtosecond High Power Laser Chemistry 飛秒超強光

雷射化學之研究

I. 1 Introduction

Femtosecond high-power laser has become a very useful experimental technique for studying the ionization or/and dissociation of atoms and molecules, high harmonic generation, creation of super-excitation in atoms and molecules, and attosecond processes. In 2002, we published a molecular theory of high-power laser ionization of molecules. Since then we have been very active in the intense-laser area. This year we have focused our attention on the high-power laser ionization-dissociation and excitation of polyatomic molecules, collaborating with experimental groups to analyze their experimental results. We hope that a new type of mass spectrometry can be developed based on the use of femtosecond high-power lasers.

I. 2 Results

Multiphoton excitation of molecules by an intense laser field is treated by us in this project [1]. When the first excitation energy is much larger than both the photon energy and the transition energy between excited states, excited states are strongly coupled with each other by photon, even though coupling with the ground state is weak. In such a case, a kind of collective excitation takes places, in which the excitation probability of every excited state is almost linear as functions of intensity on a log-log plot, and the slope is independent of the final state. By taking methane and formaldehyde as examples we numerically study this process.

Quantum chemical calculations of the geometric structure, vertical excitation energies, and ionization potentials for the isomeric pair of 1,3- and 1,4-cyclohexadienes and their mono- and dications have been performed employing a variety of theoretical methods and basis sets[2]. The computed ionization potentials and electronic excitation energies are used to evaluate the range of internal energies available for fragmentation of the cations following multiphoton resonance ionization of the cyclohexadienes in intense laser field[2]. The conditions governing the competition between multiple ionization and decomposition of the ions are also discussed. Calculations of stationary points on the potential energy surfaces for various fragmentation channels and relative product yields at different available internal energies are then utilized to analyze the trends in branching ratios of major dissociation products of the 1,4-cyclohexadiene(2+) dication, which include $C_3H_3^+ + C_3H_5^+$, $C_2H_3^+ + C_4H_5^+$, and $C_4H_3^+ + C_2H_5^+$.

The ionization/dissociation mechanism of cyclopentanone has been experimentally investigated in molecular beam by irradiating with intense 394 and 788 nm laser fields with pulse duration of 90 fs by Ding's group[3]. The range of laser intensities varied from 3×10^{13} to 4×10^{14} W/cm². For both wavelengths, the singly charged parent ion is observable while the doubly charged one cannot be found easily, although the fragmentation pattern supports its presence. Meanwhile, the extent of fragmentation at 788 nm is less than that in the 394 nm case. In collaboration with Ding's group, we quantitatively analyze the ionization processes of

cyclopentanone in intense femtosecond laser by comparing the calculation results of ionization rate constants obtained from Ammosov-Delone-Krainov, Keldysh, and Keldysh-Faisal-Reiss (KFR) theories based on hydrogenlike atom model. We also compare the experimental and theoretical results; our generalized KFR theory is found to be useful in predicting the ionization yields of singly and doubly charged cyclopentanone ion. To interpret the dissociation patterns of the cyclopentanone ions, we have used the Rice-Ramsperger-Kassel-Marcus theory with the potential surfaces obtained from the ab initio quantum chemical calculations[3].

Ionization and dissociation mechanisms of pyrrolidine in intense 800 nm laser field (10^{13} to 10^{14} W/cm²) have been experimentally investigated by Ding's group using a method of molecular beam and time-of-flight mass spectrometer[4]. Singly charged parent ion and numerous fragment ions are observed in the mass spectra, which are investigated as a function of laser intensity and polarization. In order to understand the details of the ionization processes of pyrrolidine in intense femtosecond laser field, in collaboration with Ding's group we quantitatively calculate the rate constants and ion yields by means of our generalized Keldysh-Faisal-Reiss theory, and the excitation probabilities of the excited states are also calculated by using Floquet theory[4]. The results suggest that the ionization might occur partially through the excited states of neutral pyrrolidine. Comparing with linearly polarized (LP) laser field, we observe some enhancement of fragmentation with a circularly polarized (CP) laser field above the saturation threshold intensity which might be explained by the active energies of the pyrrolidine molecular ions to be different under CP and LP laser irradiated. To interpret the dissociation patterns of the pyrrolidine ions, we have used the Rice-Ramsperger-Kassel-Marcus theory with the potential surfaces obtained from the ab initio quantum chemical calculations[4].

The mechanisms of ionization and dissociation of cyclohexanone (C₆H₁₀O) in a 90 fs, 788 nm linearly polarized laser field ranging from 10^{13} to 10^{14} W/cm² by a time-of-flight mass spectrometer (TOF-MS) have been investigated. The ion yields as a function of laser intensity have been measured experimentally. By comparison with the Ammosov-Delone-Krainov (ADK) theory based on a hydrogen-like model, the ionization mechanism of cyclohexanone in this intense femtosecond laser field has been understood. Considering the importance of molecular nuclear motions, we propose that the Franck-Condon (F-C) factor can provide the excess vibrational energy in the molecular ion. This energy is required for the decomposition of the molecular ion which finally results in the observed mass spectrum[5].

I. 3 Discussion

In the femtosecond high-power laser ionization-dissociation of polyatomic molecules, there are two types of molecular dissociation involved, one appearing within the femtosecond pulse duration(usually ~ 100 fs) and the other taking place after the laser pulse duration(that is >100 fs). In this year's work, we only consider the second type of molecular dissociation because in this case the RRKM theory can be used, which assumes that the intramolecular vibrational relaxation(IVR) is much faster than the dissociation of molecules so that the intramolecular vibrational equilibrium is established before the molecule decomposes(that is, the so-called statistical theory). This is valid for the laser intensity $I=10^{12}$ - 10^{14} w/cm². Above this range, the first type of laser-induced dissociation becomes significant. In this case, the potential surfaces of molecules can be modified by the applied laser field and the molecule decomposes easily within

100fs. This type of molecular dissociation is, of course, much more difficult to treat but we begin to study this problem.

I. 4 Reference

1. “Highly multiphoton molecular excitation by an intense laser pulse”, Y. Teranishi, M. Hayashi, F Kong, S. L. Chin, S. D. Chao, H. Mineo, and S. H. Lin, *Molecular Physics*, Volume 106, Issue 2, 333 - 339, 2008
2. “Theoretical study of multiphoton ionization of cyclohexadienes and unimolecular decomposition of their mono- and dications”, T. S. Zyubin, A. M. Mebel, M. Hayashi, S. H. Lin, *Phys. Chem. Chem. Phys.* 10(17), 2321-2331, 2008.
3. “Experimental and theoretical investigations of ionization/dissociation of cyclopentanone molecule in a femtosecond laser field”, Qiaoqiao Wang, Di Wu, Mingxing Jin, Fuchun Liu, Feifei Hu, Xihui Cheng, Hang Liu, Zhan Hu, Dajun Ding, H. Mineo, Y. A. Dyakov, A. M. Mebel, S. D. Chao, and S. H. Lin, *J. Chem. Phys.* 129, (2008) 204302.
4. “Ionization and Dissociation Processes of Pyrrolidine in Intense Femtosecond Laser Field”, Q. Wang, D. Wu, D. Zhang, M. Jin, F. Liu, H. Liu, Z. Hu, D. Ding, H. Mineo, Y. A. Dyakov, Y. Teranishi, S. D. Chao, A. M. Mebel, and S. H. Lin, *J. Phys. Chem. C*, **113**(27): 11805, 2009.
5. “Molecular Ionization of Cyclohexanone in Femtosecond Laser Fields: an Application of ADK Theory”, Q. Wang, H. Mineo, D. Wu, M. Jin, C. H. Chin, Y. Teranishi, S. D. Chao, D. Ding, and S. H. Lin, *Laser Physics*, **19**(8): 1671, 2009.

Part II. Investigations of Photophysics of Organic Solar Cells 有機太陽能電池

光物理之研究

II. 1 Introduction

We have been interested in theories of photophysical processes and molecular spectroscopies for a great number of years. Due to the rapid development of ab initio calculations it has become possible to obtain good quality of potential surfaces not only for ground electronic state but also for lower excited electronic states. In last several years, we have engaged in this effort. This year we chose to study pyrazine, an important molecule in biology.

It is well known that the anharmonic effect is important in chemistry. Taking advantage of the ability of obtaining the anharmonic potential surfaces from ab initio calculations, recently we have initiated the investigations of the anharmonic effect on unimolecular reactions through the use of the RRKM theory, and absorption and emission spectra and photophysical processes.

II. 2 Results

Ultrafast time-resolved transient absorption technique is used to investigate the thickness dependence of acoustic phonon modes of silver nanoprisms with two thicknesses, 7.8 ± 1.2 and 8.5 ± 0.69 nm, and a similar bisector length of 31.4 similar to 31.6 nm. Coherent acoustic phonon signals are observed. A new acoustic phonon frequency within 7.81 cm^{-1} similar to 11.7 cm^{-1} is found and this phonon mode is associated with the thickness of the nanoprism. Another phonon frequency between 1.95 cm^{-1} and 1.71 cm^{-1} is also observed, and its origin can be associated with the bisector length of the nanoprism[1]

We report[2], for the first time, a direct observation of the super-excited states of CH₄ in femtosecond intense laser fields using a pump (800 nm)-probe (1338 nm) technique. An unambiguous depletion of the CH (A (2) Delta -> 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.

We examined photoinduced ultrafast structural dynamics such as coherent acoustic waves in many shapes of fcc metallic nanomaterials[3]. Experimental data of nanosized thin films, prisms, spheres, rods, disks and pyramids from transient optical absorption/reflectance measurements were analyzed based on a combined Fermi-Pasta-Ulam model and two-temperature model. This work elucidates the structural dynamics induced by femtosecond laser heating, its size and shape effects on the period and phase of the excited acoustic phonon modes.

Making use of a set of quantum chemistry methods, the harmonic potential surfaces of the ground state (S-0((1)A(g))) and the first (S-1(B-1(3u))) excited state of pyrazine are investigated, and the electronic structures of the two states are characterized[4]. In the present study, the conventional quantum mechanical method, taking account of the Born-Oppenheimer adiabatic approximation, is adopted to simulate the absorption spectrum of S-1(B-1(3u)) state of pyrazine. The assignment of main vibronic transitions is made for S-1(B-1(3u)) state. It is found that the

spectral profile is mainly described by the Franck-Condon progression of totally symmetric mode $\nu(6a)$. For the five totally symmetric modes, the present calculations show that the frequency differences between the ground and the S-1(B-1(3u)) state are small. Therefore the displaced harmonic oscillator approximation along with Franck-Condon transition is used to simulate S-1(B-1(3u)) absorption spectra. The distortion effect due to the so-called quadratic coupling is demonstrated to be unimportant for the absorption spectrum, except the coupling mode $\nu(10a)$. The calculated S-1(B-1(3u)) absorption spectrum is in reasonable agreement with the experimental spectra[4].

It is well-known that the mirror image between absorption and fluorescence spectra is held for the displaced harmonic-oscillator system, and also this mirror image is independent of the chiral symmetry in which the excited-state potential energy surface is right-handed or left-handed with respect to the ground-state potential energy surface. As the first-order approximation of anharmonic correction is added into the displaced harmonic oscillator, this mirror image is broken down, and then the spectra can be depended on the chiral symmetry mentioned above. Both absorption and fluorescence coefficients are derived analytically within the first-order anharmonic approximation and numerical test is carried out to demonstrate the breaking down of the mirror image. Based on the same analysis, the electron transfer rate is derived analytically within the first-order anharmonic approximation. This rate might take the form of Arrhenius's equation but not the form of Marcus's equation. Furthermore, it is found that this rate is also depending on the chiral symmetry[5].

The equilibrium geometry and 24 vibrational-normal-mode frequencies of the excited state S2(1B2u) of pyrazine are calculated and characterized using the complete active space self-consistent field method in the adiabatic representation. The displaced harmonic oscillator approximation is used to simulate the absorption spectrum of the S2(1B2u) state along with the Franck-Condon approximation. It is found that the totally symmetric mode plays the most important role and this exactly agrees with the experimental observations. The simulated absorption spectrum agrees well with those experimentally observed. This indicates that the present S2(1B2u) state calculated in the adiabatic representation effectively includes contribution from the diabatic vibronic coupling through the conical intersection[6].

It is the purpose of the present project to study the dynamics underlying a three-pulse photon-echo process performed on a vibronic system coupled to non-Markovian baths, when a neighboring level enters into the global dynamical evolution because of broadband excitation required in these experiments[7]. Particular emphasis is on the energy gap between the vibronic levels, but also on the fluctuation amplitudes and correlation times of their corresponding thermal baths. The photon-echo signal appears to be very sensitive to the additional interfering contributions introduced by the neighboring vibronic level. It is shown that these contributions associated to the pathways involving different vibronic states are modulated by their corresponding energy gap. As a consequence, these contributions to the integrated photon-echo signal strongly decrease for large energy gaps. Also, an oscillating behavior is observed on the time dependence of the photon-echo signal resulting from the summation of the contributions provided by the individual vibronic levels. Moreover, the influence of the non-Markovian character of the baths, accountable for inhomogeneous broadening, affects the amplitude and the time dependence of the photon-echo signal, as well as its dependence with the delay time of the

laser pulses. Of course, for longer times a Markovian dynamical evolution is recovered[7].

We have observed rotationally resolved ultrahigh-resolution fluorescence excitation spectra of the 0(0)(0) (a-type) and 0(0)(0)+467 cm⁻¹ (b-type) bands of the S-2 (1)A(1)← S-0 (1)A(1) transition of jet-cooled azulene. The observed linewidth is 0.0017 cm⁻¹, which corresponds to the lifetime of 3.1 ns in the S-2 state. Zeeman splitting of rotational lines is very small so that intersystem crossing to the triplet state is considered to be very slow. Inertial defect is very small and the molecule is considered to be planar in the S-0 and S-2 states (C_{2v} symmetry). Rotational constants of the S-2 state are almost identical to those of the S-0 state, indicating that geometrical structure is similar in both electronic states. In this case, internal conversion (IC) by vibronic coupling is thought to be inactive. Therefore, the main radiationless transition process in the S-2 (1)A(1) state of azulene was identified to be IC to the S-1 B-1(2) state. However, this S-2 → S-1 IC is still slower than that of conventional polycyclic aromatic hydrocarbons. We consider it to be due to the shallower potential energy curve in the S-1 B-1(2) state, which is also responsible for the extraordinarily fast S-1 → S-0 IC in the isolated azulene molecule[8].

II. 3 Discussion

In internal conversions between higher excited electronic states (for example, between S₂→S₁) conical intersections often involve in internal conversion. In this case, the conventional theory of IC does not work near the CI point. In this project we begin to attempt to develop a theory of IC involving CI by using the IC between S₂→S₁ of pyrazine as an example. Our starting point is to use the diabatic surfaces S₂ and S₁ of pyrazine to obtain the new adiabatic surfaces in which the singularity disappears and to use these new surfaces to calculate IC.

II. 4 Reference

1. "Ultrafast Spectroscopy Studies on Thickness Dependence of Acoustic Phonon Modes in Silver Nanoprisms", P. Yu, Y. J. Shiu, Y.-T. Chen, S.-H. Lin, *JCCS* 55, 23-28, 2008
2. "Direct observation of super-excited states in methane created by a femtosecond intense laser field", A Azarm, H L Xu, Y Kamali, J Bernhardt, D Song, A Xia, Y Teranishi, S H Lin, F Kong and S L Chin, *J. Phys. B: At. Mol. Opt. Phys.* 41 (2008) 225601.
3. "Photoinduced Structural Dynamics in Laser-Heated Nanomaterials of Various Shapes and Sizes", P. Yu, J. Tang, S. H. Lin, *J. Phys. Chem. C*, 112(44):17133-17137 (2008)
4. "Theoretical study on S-1(B-1(3u)) state electronic structure and absorption spectrum of pyrazine", He RX, Zhu CY, Chin CH, Lin SH, *SCIENCE IN CHINA SERIES B-CHEMISTRY*, 51(12):1166-1173 (2008)
5. "Theoretical treatment of anharmonic effect on molecular absorption, fluorescence spectra, and electron transfer", C. Zhu, K. K. Liang, M. Hayashi, S. H. Lin, *Chemical Physics*, 358: 1-2, 137-146 (2009)
6. "Ab initio studies of excited electronic states S₂ of pyrazine and Franck-Condon simulation of its absorption spectrum", Rongxing He, Chaoyuan Zhu, C. H. Chin, S. H. Lin, *Chemical Physics Letters*, 476, 19-24 (2009)
7. "Influence of neighboring levels in three-pulse photon-echo processes", Villaeys AA, Dappe YJ, Liang KK, Lin SH, *Phys. Rev. A*, 79(5):Art. No. 053418 (2009)

8. “Rotationally resolved ultrahigh-resolution laser spectroscopy of the S-2 (1)A(1)← S-0 (1)A(1) transition of azulene”, Semba Y, Yoshida K, Kasahara S, Ni CK, Hsu YC, Lin SH, Ohshima Y, Baba M, J. Chem. Phys., 131(2): Art. No. 024303 (2009)