

# 飞秒泵浦-探测质谱方法研究苯内转换动力学\*

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**摘要:** 以飞秒 400 及 266 nm 激光脉冲结合泵浦-探测飞行时间质谱方法研究了苯  $S_2$  态内转换动力学. 400 nm 双光子过程将苯分子激发到  $S_2$  电子态, 布居在  $S_2$  电子态的分子由于能级耦合无辐射弛豫到  $S_1$  电子态. 通过测定  $C_6H_6^+$  讯号强度随泵浦-探测延迟时间的改变, 获得苯  $S_2$  及  $S_1$  电子态的衰减寿命分别为  $(48 \pm 1)$  fs 及  $(6.5 \pm 0.2)$  ps,  $S_2$  态及  $S_1$  电子态的消激发机理被认为是相应势能面间的锥形交叉引起的内转换.

**关键词:** 寿命; 泵浦-探测; 内转换

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## Internal Conversion Dynamics of Benzene Studied by Femtosecond Pump-probe Mass Spectroscopy\*

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**Abstract** The detection of benzene photoions in pump-probe experiments with the femtosecond laser pulse at 400 and 266 nm has allowed to study the dynamics of the internal conversion after excitation to the electronic  $S_2$  state. For the  $S_2$  state, an extremely short lifetime  $\tau_{D1} = (48 \pm 1)$  fs has been obtained, whereas the lifetime  $\tau_{D2} = (6.5 \pm 0.2)$  ps of the  $S_1$  state populated by the internal conversion from the  $S_2$  state is longer than that of the  $S_2$  state. The deactivation of the  $S_2$  state as well as the  $S_1$  state has been explained by the internal conversion to lower electronic states caused by the conical intersection of the corresponding potential surfaces.

**Key words** Life time, Pump-probe, Internal conversion

### 1 Introduction

Benzene is one of the important organic compounds in nature and can be considered as a model compound for a wide class of aromatic hydrocarbons. The exploration of the photophysics and photochemistry associated with the excited states of benzene has been a subject of continued interest over decades<sup>[1]</sup>. Benzene has the  $D_{6h}$  symmetry. The  $\pi$  orbitals of benzene are the most loosely bound orbitals. Therefore the ground

state as well as lowest excited states are determined by them. There are six  $\pi$  electrons in the ground state of benzene. The electronic configuration is:

$$\dots(a_{2u})^2(e_{1g})^4; S_0^1A_{1g}$$

The first excited states are obtained by taking an electron from the  $e_{1g}$  orbital and putting it in the next higher orbital  $e_{2u}$ . The configuration so obtained,  $(a_{2u})^2(e_{1g})^3(e_{2u})^1$ , yields six states:  ${}^3B_{1u}$ ,  ${}^3B_{2u}$ ,  ${}^3E_{1u}$ ,  ${}^1B_{1u}$ ,  ${}^1B_{2u}$ ,  ${}^1E_{1u}$ . Among them, four states  ${}^3B_{1u}$ ,  ${}^1B_{1u}(S_2)$ ,  ${}^1B_{2u}(S_1)$ ,  ${}^1E_{1u}$  are identified in the ultravi-

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olet absorption spectrum<sup>[2,3]</sup>.

In polyatomic molecules and molecule clusters internal conversion ( IC ) of the electronic excitation energy to vibronic levels of lower electronic state plays a dominant role in the deactivation process of highly excited states<sup>[4-6]</sup>. The dynamics of benzene molecules is characterized by ultrafast process of dissociation in combination with the internal conversion. Although the integrated absorption of the  $S_2 \leftarrow S_0$  electronic transition is quite large , the quantum yield of fluorescence from the  $S_2$  state is extremely low , indicating the existence of a very efficient internal conversion pathway to the lower electronic states<sup>[7]</sup>. Non-radiative relaxation of the second excited singlet state of benzene  $^1B_{1u}(S_2)$  is known to be extremely rapid<sup>[8]</sup>. It has been shown in a series of recent investigations that higher vibrational levels of  $S_2$  state are deactivated very fast by internal conversion<sup>[9,10]</sup>. The lifetime obtained by them for the  $S_2$  state is about 50 fs.

In this article we discuss the results of femtosecond pump-probe experiments which allow to follow the internal conversion from the primarily excited  $S_2$  state to lower electronic states in real time. The idea of the experiment can be described as follows : A femtosecond laser pulse excites benzene molecules into vibrational levels of the  $S_2$  state. Because of IC , some molecules will redistribute the vibrational energy into a new distribution of states , thus yielding a set of vibrationally equilibrated levels. A probe pulse ionizes the molecules from  $S_2$  and the redistributed states by resonant multiphoton absorption. Because the  $S_2$  state and the redistributed levels are ionized by the probe , the ion current signal may display a biexponential behavior in the delay time between the pump and probe pulses. Details of the transient behavior will depend on the ratios of ionization cross sections of  $S_2$  state and the redistributed levels and on the relative depletion rates. Hence the lifetimes can be measured directly. The energetics pertinent to our experiments is illustrated in Fig. 1. In our experiments the lifetimes of (  $48 \pm 1$  )fs for the  $S_2$  state and (  $6.5 \pm 0.2$  )ps for the  $S_1$  state are resolved.

## 2 Experimental

The laser system has been introduced in previous

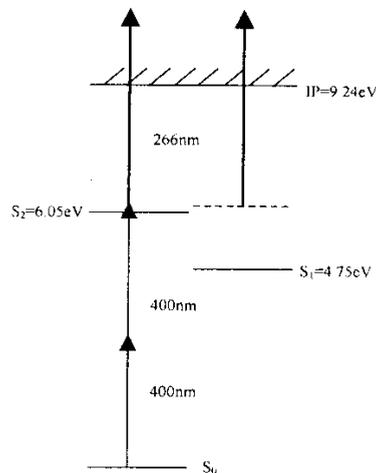


Fig. 1 Schematic energy scheme of benzene

work<sup>[11]</sup>. Briefly , it consists mainly of a seed oscillator and a regenerative amplifier with a stretcher and compressor. The oscillator is a 5 W  $Ar^+$  laser pumped self-mode-lock Ti : sapphire laser ( 20 ~ 30 fs , 86 MHz , centered at 800 nm ). Output of this oscillator is directed into a regenerative Ti : sapphire amplifier pumped by 3 kHz Nd : YAG laser ( 5 mJ/pulse at 532 nm ). The final output from the amplifier is a 3 kHz train of fundamental pulses ( 80 fs , 800 nm , 200  $\mu$ J/pulse , 400 ~ 600  $cm^{-1}$  bandwidth ).

To produce the pump and the probe pulse , we proceed in the following way. The fundamental output is frequency doubled by a  $\beta$ -BaB<sub>2</sub>O<sub>4</sub> crystal ( BBO , type I ) to produce the second harmonic generation ( SHG ) pulse , centers at about 400 nm. The output of BBO I is separated into fundamental and SHG lines. These two beams are then overlapped spatially and temporally into another BBO crystal ( type II ) to generate the third harmonic generation ( THG ). The THG output centers at about 266 nm. The residual SHG in the BBO II output is then directed into a delay-stage , while the THG light is introduced into the time-of-flight mass spectrometer ( TOF MS ) via a 29 cm focus lens and a fused silicon window. The time-delayed SHG is focused by a 26 cm focus lens and collinearly aligned with THG into the TOF MS. Typical power values of the SHG and THG beams in front of the window are about 20 and 2 ~ 3  $\mu$ J , respectively.

The TOF MS is a homemade Wiley-McLaren type machine. It consists of a beam source and a main

chamber, both of which are pumped by turbo pumps. The gaseous benzene is introduced into the beam chamber via a vitreous capillary array in the form of continuous leak. The distance from the nozzle to the interaction region is about 2 cm. The field-free flight length is about 39 cm. Ions are detected by a micro-channel plate (MCP) detector at the end of the TOF MS. Ion signals are recorded and averaged by a computer controlled transient digitizer (STR81G, Sonix) with 1 GHz sampling rate. All measurements are performed under conditions that produce minimal ionization from either the 400 nm pump or the 266 nm probe laser alone.

### 3 Results and discussion

A small amount of  $\text{NH}_3$  was added in sample gas for calibration purpose. A typical mass spectrum in Fig. 2 shows that there are four peaks of ions observed in our experiments, corresponding to  $\text{NH}_3^+$ ,  $\text{C}_3\text{H}_3^+$ ,  $\text{C}_4\text{H}_4^+$  and  $\text{C}_6\text{H}_6^+$  parent ions. The ion signal intensity was measured as a function of the time delay between a femtosecond pump pulse at 400 nm and a probe pulse at 266 nm. Because of the weakness of the  $\text{C}_3\text{H}_3^+$  and  $\text{C}_4\text{H}_4^+$  signal, we monitored pump-probe transients of  $\text{NH}_3^+$  and  $\text{C}_6\text{H}_6^+$  parent ions mainly. The investigation for the mechanism of fragment ions  $\text{C}_3\text{H}_3^+$  and  $\text{C}_4\text{H}_4^+$  is in progress. Power dependence experiments show that  $\text{C}_6\text{H}_6^+$  parent ions come from one-photon absorption of the probe pulse. The time-dependence ion signals are represented in Fig. 3 for  $\text{NH}_3^+$  and Fig. 4 for  $\text{C}_6\text{H}_6^+$ . The time-dependent population of the molecular states obtained by numerical solution of the Bloch equations are convoluted with the time-dependence of the probe pulse intensity to account for the incoherent ionization process. For known laser pulses with a Gaussian shape and the pulse duration (FWHM), we can determine the decay time of the excited state by fitting the theoretical model curve to the measured ion signals<sup>[12]</sup>.

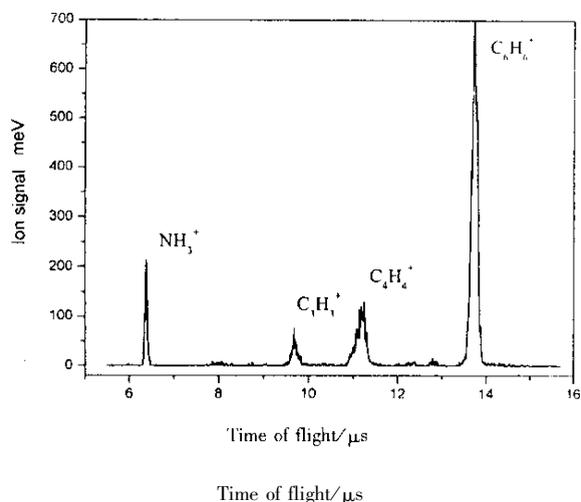


Fig. 2 TOF mass spectrum at zero delay time

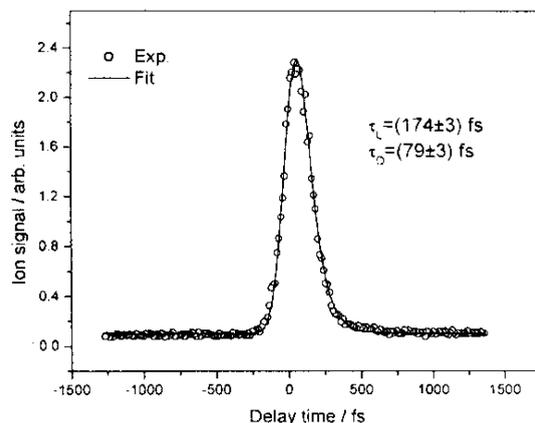


Fig. 3 Experimental ( symbols ) and fit ( solid ) lines of  $\text{NH}_3^+$

Fig. 3 displays the pump probe transient of  $\text{NH}_3^+$  for excitation at 400 nm and probing at 266 nm. The ionization potential of  $\text{NH}_3$  is 10.185 eV<sup>[13]</sup>. Therefore

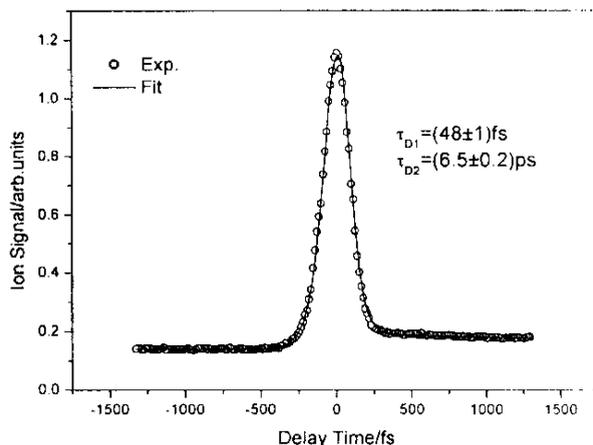


Fig. 4 Experimental ( symbols ) and fit ( solid ) lines of  $\text{C}_6\text{H}_6^+$

these  $\text{NH}_3$  molecules are photoionized by the absorption of two pump photons at 400 nm and one probe photon at 266 nm with the total energy of 10.85 eV. In these measurements, the two photons of the 400 nm pump pulse excite  $\text{NH}_3$  molecules to vibrational levels in the  $\bar{A}$  state, which is a fast predissociative state and has a lifetime smaller than 100 fs<sup>[14]</sup>. The decay of the  $\text{NH}_3^+$  in Fig. 3 shows that this is an exponential decay process and has a lifetime of  $(79 \pm 3)$  fs. The measured halfwidth of this curve of  $(174 \pm 3)$  fs corresponds to a pulse length  $\tau_L = 123$  fs at 400 nm as well as 266 nm assuming Gaussian pulse shapes for both pulses. Using this molecule with known parameters for calibration we were to determine the zero delay time and the cross correlation curve of the used laser pulses independently.

In contrast to  $\text{NH}_3^+$  for the two-photon at 400 nm excitation in  $\text{C}_6\text{H}_6^+$ , a distinctly different pump probe transient is observed. The decay of  $\text{C}_6\text{H}_6^+$  in Fig. 4 is clearly non-exponential. Approximating the decay as biexponential and using a Gaussian pulse convolution, we obtained the two time constants using non-linear least-squares regression. For the transient in Fig. 4,  $\tau_{D1} = (48 \pm 1)$  fs and  $\tau_{D2} = (6.5 \pm 0.2)$  ps. That is, for the decay of  $\text{C}_6\text{H}_6^+$ , a fast and a slow decay component were observed. The slow decay component suggests that there exists a longer lifetime state from which the ionization by one-photon probe pulse absorption is possible. The absorption of two pump photons at 400 nm with total energy of 6.2 eV excites benzene molecules to the  $S_2$  state, which locates at 6.05 eV. The lifetime obtained for the  $S_2$  state of benzene is 50 fs by Radloff *et al.* using two-color femtosecond pump-probe ion detection<sup>[3,10]</sup>. A complete lack of observed fluorescence after excitation in the region of the  $S_2$  state<sup>[7]</sup>, as well as evidence from the work of Radloff *et al.* indicates the nonradiative process responsible for this extremely short lifetime of the  $S_2$  state has been proposed to be the IC to either the  $S_1$  state or the ground state. The ionization potential of benzene is 9.24 eV. The absorption of one more photon of probe pulse at 266 nm from the  $S_2$  state results in ionization to be  $\text{C}_6\text{H}_6^+$  with the total energy of 10.85 eV. For the

lower electronic states of benzene, only the  $S_1$  state population located at 4.75 eV can be monitored with the probe photon in the one-photon absorption process.

With respect to the spectroscopic results discussed above, the very fast initial decay of the ion signals for  $\text{C}_6\text{H}_6^+$  is attributed to the internal conversion from the initially excited  $S_2$  state to the  $S_1$  as well as  $S_0$  state. The very fast decay of the two-color signal reflects the fast rates for the internal conversion from the  $S_2$  state to the lower electronic states. On the longer time scale, we observed a slowly decreasing signal with a time constant of about 6.5 ps which may be understood as due to the internal conversion from the  $S_1$  state to the  $S_0$  state followed by fragmentation. The power dependence experiments show that  $\text{C}_6\text{H}_6^+$  comes from the ionization of one-photon probe laser. So the internal conversion from the primarily excited  $S_2$  state levels to the  $S_1$  state levels with moderate vibrational energy allows for ionization by the high-energy probe photon at 266 nm, but for the  $S_0$  state, energy of one-photon at 266 nm is insufficient to ionize these molecules. Because the highly vibrationally excited ground state is not ionized under our experimental conditions, the observed ion signal at long delay time must correspond to an intermediate, the  $S_1$  state, in the overall IC to the ground state. The decay time measured in this work for the  $S_2$  and  $S_1$  states of benzene is comparable with the value of 50 fs for the  $S_2$  state and 5 ~ 10 ps for the  $S_1$  state obtained by Radloff *et al.*<sup>[10]</sup>. The potential-energy surfaces of the  $S_1$  and  $S_2$  states of benzene have been investigated using *ab initio* method<sup>[11]</sup>. This *ab initio* investigation explicitly maps out the conical intersection of the lowest  $\pi\pi^*$  excited single state with the  $S_0$  state in two dimensions. This conical intersection is of central importance for the microscopic description of the ultrafast IC dynamics in benzene.

## 4 Conclusions

This work demonstrates the utility of time-resolved multiphoton ionization with femtosecond lasers as a sensitive technique for the study of ultrafast dynamics. Applying the pump-probe technique with femtosecond laser pulse, we measured the ultrafast decay rate of benzene that was excited to the  $S_2$  state by 400 nm

photons in a two-photon absorption process. We observed a fast internal conversion with a time constant of about 48 fs leading to vibrationally excited levels in the  $S_0$  as well as  $S_1$  state. The fraction of molecules relaxed to the  $S_1$  state can be ionized by the absorption of one more 266 nm photon whereas the parallel loss channel to the  $S_0$  state cannot be observed because ionization by the one-photon probe pulse at 266 nm is impossible. The molecule population in the  $S_1$  state decreases slowly with a time constant of about 6.5 ps. The eventual decay of our photoionization signal of the  $S_1$  state is expected to be due to the IC to the ground electronic state. These results show the importance of time-of-flight mass discrimination and the ability of femtosecond resolution to separate the different dynamical channels in real time.

### References

- [ 1 ] Sobolewski A L , Woywod C , Domcke W. *J. Chem. Phys.* , 1993 , **98** :5627
- [ 2 ] Herzberg G. *Electronic Spectra and Electronic Structure of Polyatomic Molecules* , Van Nostrand , Princeton , 1966.
- [ 3 ] Radloff W , Freudenberg Th , Ritze H H , Stert V , Noack F , Hertel I V. *Chem. Phys. Lett.* , 1996 , **261** :301
- [ 4 ] Seel M , Domcke W. *J. Chem. Phys.* , 1991 , **95** :7806
- [ 5 ] Seidner L , Stock G , Domcke W. *Chem. Phys. Lett.* , 1994 , **228** :665
- [ 6 ] Farmanara P , Steinkellner O , Wick M T , Wittmann M , Korn G , Stert V , Radloff W. *J. Chem. Phys.* , 1999 , **111** :6264
- [ 7 ] Hirayama F , Gregory T A , Lipsky S. *J. Chem. Phys.* , 1973 , **58** :4696
- [ 8 ] Sekreta E , Owens K G , Reilly J P. *Chem. Phys. Lett.* , 1986 , **132** :450
- [ 9 ] Radloff W , Freudenberg Th , Ritze H H , Stert V , Weyers K , Noack F. *Chem. Phys. Lett.* , 1995 , **245** :400
- [ 10 ] Radloff W , Stert V , Freudenberg Th , Hertel I V , Jouvett C , Dedonder-Lardeux C , Solgadi D. *Chem. Phys. Lett.* , 1997 , **281** :20
- [ 11 ] Yin S H , Liu H P , Zhang J Y , Jiang B , Xu D L , Wang L , Sha G H , Lou N Q. *Chem. Phys. Lett.* , 2002 , **356** :227
- [ 12 ] Liu H P , Yin S H , Zhang J Y , Jiang B , Wang L , Lou N Q. *Chin. J. Chem. Phys.* , 2002 , **15** :213
- [ 13 ] Ashfold M N R , Langford S R , Morgan R A , Orr-Ewing A J , Western C M , Scheper C R , de Lange C. A. *Eur. Phys. J. D* , 1998 , **4** :189
- [ 14 ] Ziegler L D. *J. Chem. Phys.* , 1987 , **86** :1703