

Data Analysis for Pump-probe Experiment with Femtosecond Pulses^{*}

Liu Hongping , Yin Shuhui , Zhang Jianyang , Jiang Bo , Wang Li^{**} , Lou Nanquan
(*State Key Laboratory of Molecular Reaction Dynamics , Dalian Institute of
Chemical Physics , Chinese Academy of Sciences , Dalian 116023*)

Abstract Various analytical physical models are presented to extract the photodissociation dynamics information from the data obtained in the femtosecond pump-probe experiment. The single- and double-component models are employed to explain the single- and double-channel dissociation of parent molecules. Another single-component model for fragment dissociation or deexcitation is also presented. All cases are explanatorily demonstrated on the pump-probe experimental data.

Key words Photodissociation , Femtosecond , Pump-probe , Data analysis

CLC number : O64 **Document code** : A

1 Introduction

The application of femtosecond pump-probe technology in the study of photodissociation can provide a fundamental understanding for the chemical reaction dynamics in real time. Recently developed laser technology can supply pulse with duration less than 5 fs ($1\text{fs} = 10^{-15}\text{s}$) meaning a positive possibility to reveal the reaction steps with high time resolution^[1] while the pump-probe technology makes the direct experimental measurements come into realization. Having deepened the way we think about chemical reaction dynamics , the field of photodissociation dynamics has grown explosively in the past few decades and now pervades virtually all areas of physical chemistry^[2,3]. Photodissociation experiments provide some of the most critical tests of the fundamental assumptions we make in calculating the rates of chemical reactions via transition state theories such as the assumption of Born-Oppenheimer approximation and the assumption of rapid intramolecular vibrational energy redistribu-

tion.

The pump-probe technology requires two laser beams , one for exciting the sample molecule into the concerned excited state and the other for probing the state or fragment products after a time delay. The delay time dependence of products ' population reflects the photodissociation process in real time. The products ' population can be interrogated by many methods^[4-6] such as simple absorption , stimulated emission pumping , laser-induced fluorescence or photofragment ionization. In our experiment , the resonant enhanced multiphoton ionization (REMPI) and time of flight mass spectrometer is employed to monitor the density variation of interested states and to identify the various species with different mass to charge ratio respectively. The pump-probe experiments for several molecules such as NH_3 , Benzene , NO_2 , OCS , CS_2 and CF_3I , etc. have been performed in our laboratory. The obtained pump-probe signal helps to reveal their photodissociation process well.

The obtained pump-probe experimental data ,

* Dedication to Professor Lou Nanquan on the occasion of his 80 's birthday. ** To whom correspondence should be addressed ,
E-mail : wangliye@dicp.ac.cn

however, often exhibit different profile patterns for different molecules, different dissociation productions and different laser wavelength and power density. The correct numerical analysis of the experimental data is vital to extracting photodissociation dynamics information. In this paper, a detailed introduction of the physical model is presented and its physical explanation is also demonstrated for the obtained pump-probe data.

2 Model for a single exponential decay process

The photodissociation process can be described as that the molecule is pumped into a selected excited state and then dissociates in the declining pump laser field. In the pump laser pulse profile, the pump and dissociation process both occurs simultaneously. This interaction process can be described by optical Bloch equations in the rotating wave approximation^[7,8]:

$$\begin{cases} \frac{d\rho_{11}}{dt} = \frac{1}{2i} \phi_{01} g(t) \chi (\rho_{01} - \rho_{10}) - \frac{\rho_{11}}{\tau_1} \\ \frac{d\rho_{00}}{dt} = -\frac{1}{2i} \phi_{01} g(t) \chi (\rho_{01} - \rho_{10}) \\ \frac{d\rho_{01}}{dt} = \frac{1}{2i} \phi_{01} g(t) \chi (\rho_{11} - \rho_{00}) - \frac{\rho_{01}}{2\tau_1} \end{cases} \quad (1)$$

where ρ_{11} , ρ_{00} represents the probability of finding the system in the excited or ground state, respectively, while $\rho_{01} = \rho_{10}^*$ describes the optically induced coherence between the ground and excited states. The total lifetime of the excited state is τ_1 , while the dephasing time is assumed to be $2\tau_1$ as is appropriate for a free molecule. The quantity $\phi_{01} = 2\pi\mu_{01} E_0/h$ describes the interaction between the transition dipole moment μ_{01} and the electronic field strength $E(t) = E_0 g(t) \cos\omega t$ of the laser pulse, where the envelope function $g(t)$ characterizes the laser pulse shape, which has been chosen to be $g(t) = [\pi \cosh(t/\tau_p)]^{-1}$. The Bloch equations (1) are solved numerically. The results obtained for $\rho_{nn}(t)$ are then convoluted with the time dependence of the probe-pulse intensity to account for the incoherent ionization process. Inserting the $\text{sech}^2(t)$ time dependence of the laser pulses, we can determine the decay time τ_1 by minimizing the difference between the measured ion signals and the theoretical fit curve. The optimum fit

can also inherently determine the zero delay time between the pump and probe pulse.

To simplify the data processing, however, the observed signal $I(t, t_0)$ is often approximated to be the convolution between the pump-probe correlation function $G(t, t_0)$ and the decay function $F(t, t_0)$,

$$I(t, t_0) = \iint G(t_1, t_0) F(t_2, t_0) \chi(t_1 + t_2 - t) dt_1 dt_2 \quad (2)$$

where, $G(t, t_0)$ is often taken as Gaussian function, $F(t, t_0)$ as exponential decay function. The optimum fit between $I(t, t_0)$ and experimental data can determine the values of the zero delay time between the pump and probe pulses, and the decay lifetime.

For multi-component decay process, the decay function $F(t, t_0)$ can be extended to be

$$F(t, t_0) = \sum_i a_i e^{-(t-t_0)/\tau_i} \quad (3)$$

where a_i , τ_i correspond to the signal amplitude and the lifetime of i th decay process, respectively.

3 Discussion

3.1 Single exponential decay process of the parent molecule's photodissociation

As described in the second part above, the single exponential decay process is very simple. Fig. 1a is the simulation for Eq.(2) with two different correlation function width parameters, $\tau_{L1} = 160$ fs, $\tau_{L2} = 260$ fs, from which we can see that when τ_L varies larger, the single exponential decay information with short lifetime $\tau_D = 100$ fs will be concealed in the correlation function profile. This is why we should compress the femtosecond pulse duration in revealing the photodissociation of molecules with short lifetime. Fig. 1b is the simulation with two different decay lifetime parameter $\tau_{D1} = 100$ fs, $\tau_{D2} = 500$ fs, where we can obtain the conclusion that the larger τ_D is, the more the peak point shifts away from the zero point. This simulation indicates that a molecule with short dissociation lifetime is preferred to calibrate the pump-probe zero delay time point, for example, the Benzene or NH_3 is often chosen as calibration molecule. In our experiment NH_3 is employed, where the pump and probe pulses are 266 nm and 400 nm respectively. The correlation width can be accurately determined to

be $\tau_L = (161 \pm 2)$ fs as well as the zero delay time point. The experimental data and the fitted line are drawn in Fig. 1c.

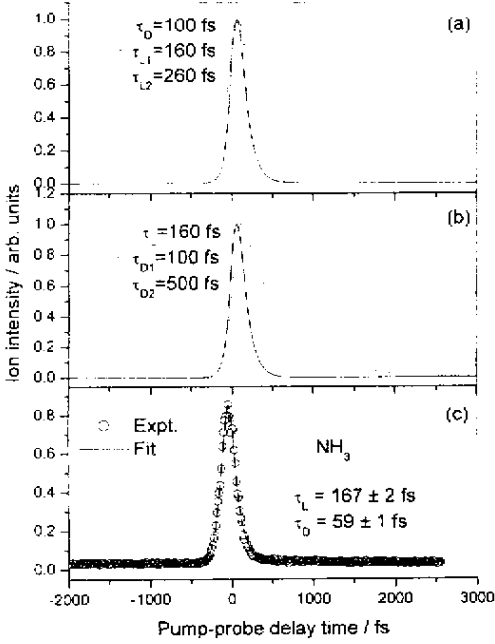


Fig. 1 (a) the simulated pump-probe signals with different correlation function width $\tau_{L1} = 160$ fs , $\tau_{L2} = 260$ fs ;
 (b) the simulated pump-probe signals with different decay parameters $\tau_{D1} = 100$ fs , $\tau_{D2} = 500$ fs ;
 (c) the experimental pump-probe signal for NH_3 and its least-squares fit.

3.2 Double exponential decay process of the parent molecule's photodissociation

This kind of double exponential decay process is often observed provided that stronger pump laser pulse is applied. In our experiment , the molecule NH_3 and Benzene both show the double decay process when 266 nm pulse varies stronger. Suppose the pump pulse excites the ground molecule into a highly excited quantum state S_2 , where two physical processes occurs , one for the molecule in S_2 state to dissociate with τ_{D2} and the other for the molecule transmit into another excited state S_1 lower than S_2 in a time scale nearly zero and then to dissociate with τ_{D1} or the S_2 state has two direct dissociation or deexcitation channels. The process in the former case is demonstrated in Fig. 2a and its simulation profile in Fig. 2b with parameters $\tau_L = 160$ fs , $\tau_{D1} = 100$ fs , $\tau_{D2} = 1000$ fs , where two decay processes can be distinguished

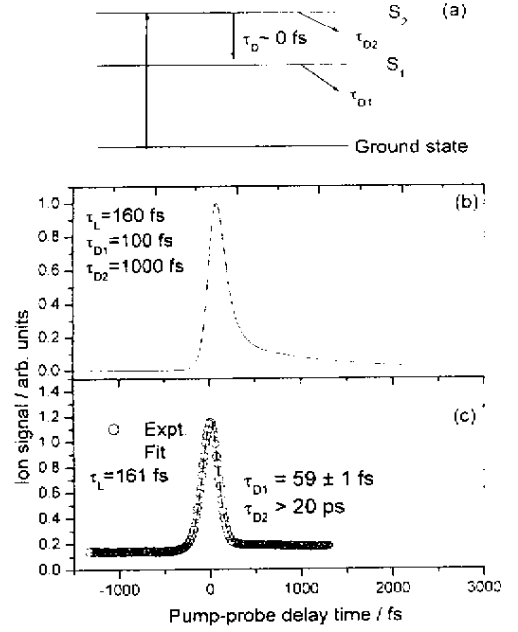


Fig. 2 (a) the schematic diagram of double-decay process ;
 (b) the simulated pump-probe signal for double-decay process with lifetime parameters $\tau_{D1} = 100$ fs and $\tau_{D2} = 1000$ fs ;
 (c) the experimental pump-probe signal for Benzene and its least-squares fit , where a long time of decay process (> 20 ps) is observed.

obviously. Fig. 2c is the pump-probe signal of Benzene obtained in our experiment. The fitted line is also drawn in Fig. 2c , which is in coincidence with the experimental data. In the forward direction , 266nm pulse-pumped Benzene dissociates through two channels with $\tau_{D1} = (59 \pm 1)$ fs , $\tau_{D2} > 20$ ps , respectively.

3.3 Single exponential decay process of the fragments

Such process is relatively complicated compared with the cases above. For simplification , we consider a simple case described below. Suppose the parent molecule dissociates by

$$F_1(t, t_0) = a_1 e^{-(t-t_0)/\tau_{D1}} \quad (4)$$

and the fragment dissociates or deexcites by

$$F_2(t, t_0) = a_2 e^{-(t-t_0)/\tau_{D2}} \quad (5)$$

then the decay process of fragment can be described by

$$f(t, t_0) = \iint [c_1 - c_2 F_1(t_1, t_0)] \times F_2(t_2, t_0) \delta(t_1 + t_2 - t) dt_1 dt_2 \quad (6)$$

Substitute Eq.(4) and (5) into the above equation ,

$$f(t, t_0) = c_1 \tau_2 + \frac{c_2}{1/\tau_{D1} - 1/\tau_{D2}} e^{-(t-t_0)/\tau_{D1}} +$$

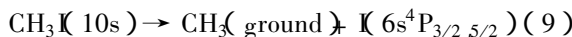
$$\left(\frac{c_2}{1/\tau_{D2} - 1/\tau_{D1}} - c_1 \tau_{D2} \right) e^{-(t-t_0)/\tau_{D2}} \\ \equiv \alpha_0 + \alpha_1 e^{-(t-t_0)/\tau_{D1}} + \alpha_2 e^{-(t-t_0)/\tau_{D2}} \quad (7)$$

According to Eq.(1), the observed signal I will be

$$I(t, t_0) = \int \int G(t_1, t_0) f(t_2, t_0) \delta(t_1 + t_2 - t) dt_1 dt_2$$

Its simulation is given in Fig. 3a, where the time parameters are taken as $\tau_L = 160$ fs, $\tau_{D1} = 100$ fs and $\tau_{D2} = 1000$ fs. This kind of signal is observed by Poth *et al.* in their CH₃I cluster pump-probe experiment for the dissociation fragments (Fig. 3b is the signal for CH₃I⁺)⁹. As the first step, the cluster molecule is pumped into the excited state and nearly at the zero delay time the parent's dissociation rate is larger than that of fragment, then the observed signal has a large value near the zero point. With the pump-probe delay time gap increasing, the deexcitation rate of the frag-

ment becomes larger and the signal decreases until reaching a lowest dip. At the delay time far away from the zero point, both processes have nearly zero decay rate, resulting in a stable signal, nearly independent on the time evolution. This is an ideal description in the asymptotic domain. In real experiment, the signal will become weaker with the time evolution. As for the CH₃I, the 270 nm pulse pumps the ground CH₃I cluster into 10s Rydberg state, and then the excited molecule dissociates through channel



This recombination product undergoes deexcitation through internal vibrational relaxation until it reaches the surface crossing with the dissociating \tilde{A} state and dissociate again with final state $P_{3/2, 5/2}$ for iodine. Their determined lifetimes are 234 fs and 1.25 ps, corresponding to the two dissociation channels above, respectively.

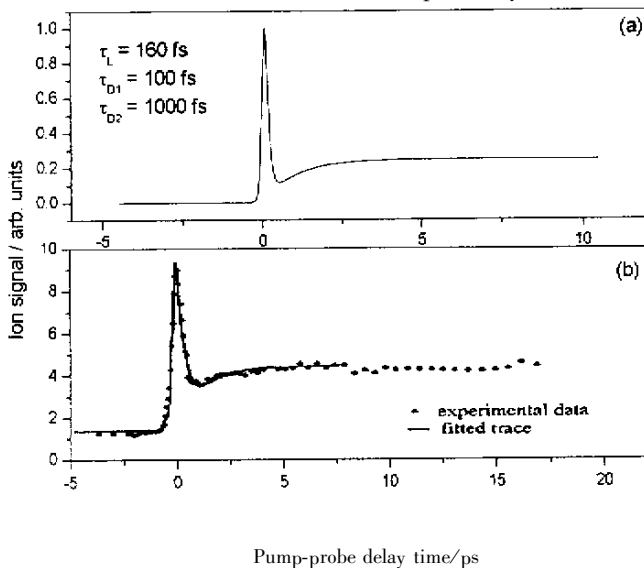


Fig. 3 (a) the simulated pump-probe signal for fragment's single-decay deexcitation ;
(b) the experimental pump-probe signal for CH₃I cluster's fragment CH₃I
and its least-squares fit^[9]

For other complicated photodissociation processes, it is difficult to present a clear physical picture in a simple model for the increasing number of parameters.

4 Conclusion

Several models are presented to describe the photodissociation decay process of the parent molecule and its fragments. Their physical explanations are al-

so made for the simulated curves and experimental data points. The nice agreement between the simulation and the experimental data indicates that the models are perfect in describing the photodissociation process.

Acknowledgements : Financial support from the NKBRFSF and NSFC Foundation (29833080, 20003012 and 29973044) and the Chinese Postdoc-

toral Foundation is gratefully acknowledged.

References

- [1] Fork R L , Greene B I , Shank C V. *Appl. Phys. Lett.* , 1981 , **38** : 671
- [2] Zwail A H. *Femtochemistry* , World Scientific , Singapore , 1994.
- [3] Okabe Cf H. *Photochemistry of Small Molecules* , Wiley , New York , 1978.
- [4] Yamanouchi K , Field R W. *Laser Chem.* , 1995 , **16** : 31
- [5] Schulz P A , Sudb A S , Krajnovich D J , Kwok H S , Shen Y R , Lee Y T. *Ann. Rev. Phys. Chem.* , 1979 , **30** : 379
- [6] Butler L J , Neumark D M. *J. Phys. Chem.* , 1996 , **100** : 12801
- [7] Feudenberg Th , Radloff W , Ritze H H , Stert V , Weyers K , Noack F , Hertel I V. *Z. Phys. D* , 1996 , **36** : 349
- [8] Farmanara P , Stert V , Radloff W. *Chem. Phys. Lett.* , 1999 , **303** : 521
- [9] Poth L , Zhong Q , Ford J V , Castleman A W. *J. Chem. Phys.* , 1998 , **109** : 4791

飞秒泵浦-探测实验数据分析*

刘红平 , 尹淑慧 , 张建阳 , 姜波 , 王利** , 楼南泉
(中科院大连化学物理研究所分子反应国家重点实验室, 大连 116023)

摘要: 陈述了几种获取飞秒泵浦-探测实验数据中的光解动力学信息的解析物理模型. 其中单分量和双分量模型用来解释母体分子的单通道和双通道解离过程, 另一个单分量模型用来解释碎片分子的解离或去激发过程. 所有模型都结合泵浦-探测实验数据予以解释.

关键词: 光解; 飞秒; 泵浦-探测; 数据分析

中图分类号: O64 文献标识码: A

* 献给楼南泉院士 80 诞辰. ** 通讯联系人, E-mail: wangliye@dicp.ac.cn