[Article]

doi: 10.3866/PKU.WHXB201311122

www.whxb.pku.edu.cn

飞秒时间分辨的光电子影像对3-甲基吡啶分子超快动力学研究

布玛丽亚·阿布力米提^{1,2,3} 朱荣淑^{1,*} 邱学军^{2,3} 秦晨^{2,3} 张冰^{2,3,*}(¹哈尔滨工业大学深圳研究生院, 环境科学与工程研究中心, 广东深圳 518055; ²中国科学院武汉物理与数学研究所, 波谱与原子分子物理国家重点实验室, 武汉 430071; ³中国科学院大学, 北京 100049)

摘要: 利用飞秒时间分辨的光电子影像技术结合时间分辨的质谱技术, 研究了3-甲基吡啶分子激发态的超快过程. 实时观察到了3-甲基吡啶分子 S_2 态向 S_1 态高振动能级的超快内转换过程, 该内转换的时间大约为 910 fs. 二次布居的 S_1 态主要通过内转换衰减到基态 S_0 , 该内转换的时间尺度为 2.77 ps. 光电子能谱分布和光电子角分布显示, S_2 态和 S_1 态在电离的过程中跟 $3p$ 里德堡态发生偶然共振. 本次实验中还用 400 nm 两个光子吸收的方法布居了3-甲基吡啶的 $3s$ 里德堡态. 研究表明, $3s$ 里德堡态的寿命为 62 fs, 并主要通过内转换快速衰减到基态.

关键词: 甲基吡啶; 光电子影像; 内转换; 泵浦-探测; 时间分辨光谱

中图分类号: O644

Studies of Ultrafast Dynamics of 3-Picoline with Femtosecond Time-Resolved Photoelectron Imaging

ABULIMITI Bumaliya^{1,2,3} ZHU Rong-Shu^{1,*} QIU Xue-Jun^{2,3} QIN Chen^{2,3} ZHANG Bing^{2,3,*}(¹Environmental Science and Engineering Research Center, Harbin Institute of Technology Shenzhen Graduate School, Shenzhen 518055, Guangdong Province, P. R. China; ²State Key Laboratory of Magnetic Resonance and Atomic and Molecular Physics, Wuhan Institute of Physics and Mathematics, Chinese Academy of Sciences, Wuhan 430071, P. R. China;³University of Chinese Academy of Sciences, Beijing 100049, P. R. China)

Abstract: The ultrafast dynamics of excited states in 3-picoline was studied using femtosecond time-resolved photoelectron imaging, coupled with time-resolved mass spectroscopy. An ultrafast internal conversion from the S_2 state to the vibrationally excited S_1 state in about 910 fs was observed. This secondary-populated S_1 state further deactivates to the S_0 state in 2.77 ps. The photoelectron energy and angular distributions show ionizations from the singlet $3p$ Rydberg states. Two 400 nm photon excitations to the $3s$ Rydberg state suggest that this state probably decays to the ground state in 62 fs.

Key Words: Picoline; Photoelectron imaging; Internal conversion; Pump-probe; Time-resolved spectroscopy

1 Introduction

Efficient electronic relaxation following absorption of ultraviolet (UV) light is crucial for photostability in biological chromophores. Understanding the microscopic details of decay pathways is thus of considerable interest.^{1,2} After absorption of

UV light, internal conversion (IC) caused by electronic non-adiabaticity and intersystem-crossing (ISC) caused by spin-orbit coupling are the two major nonradiative pathways in photoexcited polyatomic molecules.^{3–11} In polyatomic molecules excited to higher electronic states, IC to vibronic levels of lower

Received: August 29, 2013; Revised: November 12, 2013; Published on Web: November 12, 2013.

*Corresponding authors. ZHU Rong-Shu, Email: rszhu@hitsz.edu.cn; Tel: +86-755-26032557. ZHANG Bing, Email: bzhang@wipm.ac.cn; Tel/Fax: +86-27-87198491.

The project was supported by the National Natural Science Foundation of China (91121006, 21273274).

国家自然科学基金(91121006, 21273274)资助项目

© Editorial office of *Acta Physico-Chimica Sinica*

electronic states is one of the dominant mechanisms for deactivation.^{3,4} Femtosecond time-resolved photoelectron imaging (TRPEI) combined with resonance-enhanced multiphoton ionization is a novel experimental means to probe excited-state dynamics of molecules.^{5–11} In our previous work, we demonstrated this methodology in examining the 2-picoline IC.¹² The TRPEI allowed observation of ionization from the S_2 and S_1 states as a function of pump-probe time delay, thereby visualizing both the S_2 decay and the S_1 growth in real time.

Pyridine and its methyl derivatives are important heteroaromatic molecules that have attracted a great deal of attention over the last two decades because of their important roles in UV photodamage of nucleic acids.^{13–17} Compared with other pyridine derivatives, 3-picoline has been less studied by theoretical and experimental investigations.¹⁸ Previously, 3-picoline was believed to be a totally nonfluorescent molecule until 1979 when Yamazaki *et al.*¹⁸ discovered weak fluorescence in the gas phase. The fluorescence quantum yield was determined to be 5.4×10^{-5} at the S_1 0^0 level, and these yields decrease sharply as excitation energy is raised to that corresponding to the S_2 state. They suggested that such a low fluorescence quantum yield is due to IC processes.¹⁸ Although deactivation from the excited states of 3-picoline is likely IC mediated, 3-picoline has not been subjected to ultrafast time-resolved study; no direct evaluations of the excited-state decay rates of 3-picoline were performed, and so far no detailed photoelectron spectroscopy has been reported. In addition, there is scant information about the Rydberg states of 3-picoline.

In this study, we performed TRPEI on the $\pi\pi^*$ (S_2) and $3s$ Rydberg states of 3-picoline to gain insight into the electronic structure and relaxation processes.

2 Experimental details

The experimental setup employed in the present work is essentially identical to that described in our previous photoelectron imaging studies.^{19–22} Briefly, the sample gas (5% 3-picoline), seeded in a He buffer gas at background pressure of 200 kPa, is expanded through a pulsed valve to generate a pulsed molecular beam. The supersonic molecular beam is collimated by a conical skimmer and perpendicularly intersected two laser beams in a two-stage ion lens region. The generated photoelectrons are extracted into a 36-cm field-free region that is doubly shielded against stray magnetic fields by a μ -metal tube. At the end of the flight tube, the electrons are detected by a two-dimensional (2D) imaging detector comprising a microchannel plate and phosphor screen and a charge-coupled device (CCD) camera (LAVISION Inc., Imager Intense). Three-dimensional (3D) distribution reconstructions are performed using the basis-set expansion (BASEX)²³ forward convolution method.

The details of our femtosecond laser system have been described elsewhere.^{19–22} Briefly, the seed beam was generated by a commercial Ti:sapphire oscillator pumped by a continuous wave (CW) second harmonic of an Nd:YVO4 laser, and then

amplified by an Nd:YLF pumped regenerative amplifier to generate a 1 kHz pulse train centered at 800 nm (45 fs pulse width) with maximum energy of $1 \text{ mJ} \cdot \text{pulse}^{-1}$. This light was split into two equal-intensity beams, one of which was frequency tripled to 266 nm, generated in a 0.2-mm-thick BBO crystal by sum frequency mixing of the second harmonic and fundamental, to produce the pump light. The remaining 800 nm beam served as a probe light. The two laser beams were introduced into the vacuum chamber collinearly with a dichroic mirror, and focused with two fused silica lens of $f=500, 350 \text{ mm}$. During experiments, typical pulse energies were about $2.1 \text{ } \mu\text{J} \cdot \text{pulse}^{-1}$ for the pump and about $35 \text{ } \mu\text{J} \cdot \text{pulse}^{-1}$ for the probe pulse. Polarization directions of the pump and probe lasers were parallel to each other and to the face of the detector. The relative time delay between the pump and probe pulses was accurately monitored by a computer-controlled linear translation stage (PI, M-L01.4A1). The cross-correlation for the pulses of 266 and 800 nm was $(124 \pm 50) \text{ fs}$.

3 Results and discussion

3-Picoline has a broad absorption band from 240 to 280 nm and the absorption at 266 nm is relatively strong.¹⁸ Its two lowest excited electronic single states S_1 ($n\pi^*$) and S_2 ($\pi\pi^*$) were found at 288.0 nm (4.30 eV) and 267.8 nm (4.63 eV), respectively.¹⁸ The 266.0 nm pump pulse energy (4.66 eV) is just above that of the S_0-S_2 0^0 transition of 3-picoline;¹⁸ isoenergetic with it is a highly vibrationally excited state belonging to the S_1 state. Relatively poor Franck-Condon factors for the vibrationally excited S_1 state excitation were expected. Herein, it is believed that in our experiment the pump pulse excited 3-picoline mainly to its S_2 state. The probe pulse (800 nm) energetically enabled four-photon ionization from the S_1 and S_2 states. All measurements for this work were performed under conditions where the ionization signals from either the 266 nm pump or 800 nm probe laser alone were minimized.

The time-of-flight mass spectra of 3-picoline were obtained when pump and probe beams temporally overlapped. Only two peaks appear corresponding to the $\text{C}_6\text{H}_7\text{N}^+$ parent ions and $\text{C}_5\text{H}_4\text{N}^+$ ions. The area ratio of $\text{C}_6\text{H}_7\text{N}^+$ and $\text{C}_5\text{H}_4\text{N}^+$ is 35:1. Moreover, it is believed that most of $\text{C}_5\text{H}_4\text{N}^+$ originates from the dissociation of parent ion $\text{C}_6\text{H}_7\text{N}^+$, since the time profile of the $\text{C}_5\text{H}_4\text{N}^+$ is very similar to that of the parent ion $\text{C}_6\text{H}_7\text{N}^+$. Therefore, the contribution to the total photoelectron signals from the generation of $\text{C}_5\text{H}_4\text{N}^+$ can be neglected.

Fig.1 shows the time-resolved total ion signal of the parent ion formed after one-photon excitation of the S_2 state at 266 nm as a function of the pump-probe delay. The decay profiles are fitted with a single exponential decay with a lifetime of $t_1=2.77 \text{ ps}$ convoluted with a Gaussian function that describes the instrument response. The ion signal reflects the excitation and decay of the excited states of 3-picoline. As mentioned above, deactivation from the S_2 state of 3-picoline is likely IC mediated. The S_2 state perhaps decays to the S_1 and S_0 states. The ob-

Fig.1 Time-resolved total ion signal of 3-picoline parent ion as a function of delay time, between the pump pulse at 266 nm and the probe pulse at 800 nm

The circles indicate experimental results; solid line represents fitted results.

served decay profile, however, fits a single-exponential function very well; although a main decay channel in 2-picoline is IC, a fast decay component was absent in 3-picoline IC.¹² This indicates that the time dependence of the total parent ion signal in this experiment is insensitive to the electronic symmetry change induced by $S_2 \rightarrow S_1$ IC. The dynamics concealed in those ion signal decays will be discussed later in detail using an energy analysis and the angular distributions of the photoelectrons obtained from photoelectron images.

Photoelectron images are taken in a series of delay times (Δt) between the pump and probe pulses. Raw photoelectron images are reconstructed using BASEX. The BASEX-inverted photoelectron images represent a 2D slice through the centre of the original 3D photoelectron distribution. Two well-resolved concentric rings appear in the observed images as the delay time changes. The rings with different radii in the imaging correspond to photoelectrons with different kinetic energy components. Fig.2 shows a photoelectron spectrum at $\Delta t=910$ fs extracted from images following the excitation of 3-picoline with femtosecond laser light at 266 nm; a photoelectron scattering image obtained by BASEX inversion at $\Delta t=910$ fs is shown in the inset. Two well-resolved bands appearing in the photoelectron spectra correspond to the well-resolved concentric two rings in the images. These two bands are observed centered at 0.83 and 1.17 eV, and designated the 1st and 2nd bands, respectively. With the two bands exhibiting a slight sharpness, some intermediate Rydberg states most likely affect the ionization process.⁷⁻¹¹ The ionization potential of 3-picoline is determined to be 9.0 eV.²⁴ Besides these two bands, no other smaller energy bands are observed in the present experiment. Hence, the observed signals are probably due to the absorption of four photons from the ionization pulse by the excited 3-picoline. Because of the Franck-Condon overlap, the ionization transition from the low vibrational states of S_2 leads to the low vibrational states of D_0 . The maximum photoelectron energy of the 2nd band (1.87 eV) corresponds well to the difference between the total photon energy and the vertical ionization energy (1.86 eV). Therefore, the 2nd band is ascribed to ionization from S_2

Fig.2 Photoelectron spectrum at $\Delta t=910$ fs extracted from imaging following excitation of 3-picoline with femtosecond laser light at 266 nm

The photoelectron image obtained by BASEX inversion at $\Delta t=910$ fs is shown in the inset. The linear polarizations of the pump and probe lasers are aligned vertically in the plane of the imaging figure.

state. In addition, we ascribed the 1st band as ionization from the S_1 state. In principle, molecules in the S_1 state have vibrational energies that correspond to energy transitions from the S_2 state; slow electrons emerge from ionization to the vibrationally excited levels of the cation. The fact that the energy difference between the 1st and 2nd bands (0.33 eV) is nearly equal to the energy gap between the S_2 and S_1 states (0.34 eV) supports our assignment. Because only the S_2 state is believed to be excited with the pump pulse, the appearance of the first band is probably due to the population of the S_1 state due to S_2 -state IC.

To gain more information about the time evolution of these two bands, Fig.3 shows the time-resolved photoelectron kinetic energy (PKE) distributions extracted from a series of images. During 910 fs, these distributions are characterized by a sharp rise and decay in electron signal associated with the 2nd band, whereas there is only a slow growth in electron signal for the 1st band. The 1st photoelectron band also decreases after 910 fs. In Fig.3, the 1st photoelectron band shows the formation and decay of the S_1 state; the 2nd photoelectron band shows the same for the S_2 state. The photoelectron spectrum shift from

Fig.3 Photoelectron kinetic energy distributions of 3-picoline pumped at 266 nm and probed at 800 nm extracted from the images

All distributions have been normalized to the total photoelectron count.

one energy band to another is a good signature of electronic configurations changing. Thus, in accordance with the origin of these two bands, the photoelectron spectrum of the 2nd band decay and the 1st band rise is attributed to IC from the S_2 state to the S_1 state occurring within about 910 fs period. After this period, all photoelectron bands decrease slowly together. This slow decay is characterized by the time constant of 2.77 ps obtained from the total parent ion signal.

Although the time dependence of the total parent ion signal in this experiment appears insensitive to the electronic symmetry change induced by S_2 – S_1 IC, the IC from the S_2 state to the vibrationally excited S_1 state is observed by time-resolved PKE distributions. The time scale for this S_2 – S_1 IC was estimated to be about 910 fs; for 2-picoline, the time scale of S_2 – S_1 IC was measured at (937 ± 156) fs. Following IC back to S_0 , the ground state molecule will possess 4.66 eV of excess vibrational energy, but its energy is essentially unavailable during ionization because of very small Franck-Condon factors associated with the energetically accessible ion state; hence, S_2 deactivation to S_0 cannot be ruled out. As all photoelectron bands decrease slowly at similar rates after 910 fs, the populated S_2 can decay to the S_0 state by IC as well. Acquiring information about the S_2 – S_1 IC of 3-picoline from the time dependence of the total parent ion signal is difficult and can be explained by the smaller ionization cross-section of S_2 compared with that for S_1 and that only a part of the S_2 population is transformed to S_1 ; The total parent ion signal has time dependence that is insensitive to changes in electronic symmetry induced by S_2 – S_1 IC. The S_1 state probably deactivates to the S_0 state after population by S_2 – S_1 IC. Therefore, the time 2.77 ps obtained from the time-resolved total ion signal probably reflects a mixed time scale for S_2 – S_0 IC and S_1 – S_0 IC. There was no significant long-lived component observed in the present work, suggesting that the S_2 – T and S_1 – T crossing quantum yield should be negligible.

From our analysis, the two peaks in Fig.3 are sharp and no Franck-Condon overlap envelope is observed. Ionization from the Rydberg state to the cationic state obeys the propensity rule $v=0$ arising from the orthogonality of the vibrational wave functions. This makes each ionization channel appear as a single peak in the PKE distributions.^{9,10} In our previous work, 2-picoline was enhanced from the resonance between the $3p_v$ and $3p_z$ Rydberg states.¹² A similar accidental resonance is anticipated here for 3-picoline.

A more general and direct indicator of electronic character is the electronic transition dipole moment. In photoelectron spectroscopy, the transition dipole moment from a nonstationary state to the ionization continuum varies with non-adiabatic electronic transition, resulting in a variation in the photoelectron angular distributions (PADs).^{8,25,26} TRPEI produces a visualization of the time dependence of the PKE distribution and PADs simultaneously, thereby giving more information about the non-adiabatic dynamics. PADs aid the exploration of the ionization dynamics, rotational wave packet motions,^{8,22} and

the properties of low-lying Rydberg states.^{9,10,27,28} In the cylindrically symmetric system, in which the pump and probe laser polarization vectors are parallel to each other, the laboratory frame PADs at a given delay time Δt resulting from four-photon ionization can be similarly expanded as:²⁹

$$I(\theta, \Delta t) = \sigma(\Delta t) [1 + \beta_2(\Delta t)P_2(\cos\theta) + \beta_4(\Delta t)P_4(\cos\theta) + \beta_6(\Delta t)P_6(\cos\theta) + \beta_8(\Delta t)P_8(\cos\theta) + \beta_{10}(\Delta t)P_{10}(\cos\theta)] \quad (1)$$

where $\sigma(\Delta t)$ is the integral cross-section, $P_L(\cos\theta)$ is a Legendre polynomial, θ is the angle between the laser polarization direction and the direction of the ejected electron k -vector, and $\beta_L(\Delta t)$ represents the anisotropy parameter. The PADs are extracted from the inverse BASEX-transformed images. Fitting PAD data to equation (1), the anisotropy parameters at different delay times are determined. We find that the value from β_4 to β_{10} is negligible. The anisotropy parameter β_2 of the 1st and 2nd bands are (0.525–0.605) and (0.495–0.521), respectively.

For one-photon ionization of a one-electron atom, the outgoing photoelectron from an s state is a pure p wave, yielding the anisotropy value $\beta_2=2$; for other initial electron orbital angular momentum states, the anisotropy parameter is reduced because of interference between a pair of outgoing partial waves. A similar situation occurs for molecules, especially for those in atomic-like Rydberg states.^{9,10,27} The anisotropy parameters indicate that the two peaks in Fig.3 are probably associated with mixed outgoing partial waves of photoelectrons ejected from the Rydberg p orbital.

Since the energy is not enough to reach Rydberg states following the absorption of one probe photon by the excited 3-picoline, we expect that accidental resonance with some Rydberg states will occur when the excited 3-picoline absorbs two probe photons.³⁰ Photoelectron energy and angular distributions for some other azabenzenes indicated that the ionization from the S_1 state was being enhanced by the resonance with singlet $3s$ and $3p$ Rydberg states at this energy level.^{9,10,27} A similar resonance effect is also anticipated for 3-picoline. The PKE produced by the resonance with a Rydberg state is given by:²⁷

$$\text{PKE} = T_R + 2\hbar\omega_2 - \text{IP} = 2\hbar\omega_2 - \frac{R}{(n-\delta)^2} \quad (2)$$

where T_R is the term value of the Rydberg state, IP is the ionization potential, R is the Rydberg constant (13.606 eV), n is the principal quantum number of the Rydberg state, and δ is the quantum defect. For molecules composed of second-row atoms, typical δ values are 0.9–1.2 for s -orbitals, about 0.3–0.5 for p orbitals, and about 0 for d orbitals.²⁵ Recalling that the two peaks in Fig.3 are centered at 0.83 and 1.17 eV, and using equation (2) with principal quantum number 3, we then calculated the quantum defect values for the two Rydberg states to be 0.34 and 0.55. Thus, these two peaks could arise from $3p$ Rydberg states. The wavenumbers of these two Rydberg states are 54282 and 57024 cm^{-1} . Comparing the $3p$ Rydberg-state energy of 3-picoline with that of 2-picoline, we infer that the two peaks in Fig.3 could correspond to the $3p_z$ (54282 cm^{-1}) and $3p_v$ (57024 cm^{-1}) Rydberg states. All the ionization mechanisms

and IC dynamics analyzed for the 266 nm pump and 800 nm probe experiment are shown in Fig.4.

For 3-picoline, the time scale for this S_2 – S_1 IC was estimated to be about 910 fs; for 2-picoline, the time scale of S_2 – S_1 IC was measured at (937 ± 156) fs.¹² The time constants of IC of 2-picoline and 3-picoline are almost the same. Whereas, in 3-picoline, only a part of the S_2 population was transformed to S_1 , the IC of the S_2 state to the highly excited S_0 state appeared to be another channel. In 2-picoline, the IC of the S_2 state to the highly excited S_0 state was found to be negligible. However, the position of methyl group substitution may affect the relaxation behavior on the S_2 surface which was also observed on other molecules.³¹

To obtain more information about the Rydberg state of 3-picoline, a 400 nm pump and 800 nm probe TRPEI experiment was conducted. The $3s$ Rydberg state is populated following two-photon 400-nm excitation.³⁰ To measure the temporal evolution of the $3s$ Rydberg state, we projected the Rydberg wave state onto the well-studied cationic ground state with another 800 nm ionizing pulse. The total parent ion signal as a function of pump-probe delay was obtained. The powers of pump and probe pulses are modulated to make sure that no enhancement

Fig.4 Energy excitation scheme of the ground, excited and ionic states of 3-picoline

The pump laser (266 nm) prepares the S_2 state. Due to ultrafast internal conversion, this state converts to the lower-lying state S_1 with higher vibrational energy. Here, 1st and 2nd are corresponding to the first and second bands marked on Fig.2, respectively.

Fig.5 Time-resolved total ion signal of 3-picoline parent ion as a function of delay time, between the pump pulse at 400 nm and the probe pulse at 800 nm

The $3s$ Rydberg state is populated following two-photon 400-nm excitation. The circles indicate experimental results; solid lines represent fitted results.

in the signals is observed in the negative time delay direction. Fig.5 shows the time-resolved total ion signal of the parent ion formed after two-photon excitation of the $3s$ Rydberg state at 400 nm as a function of the pump-probe delay. The decay profiles are fitted with a single exponential decay convoluted with a Gaussian function that describes the instrument response. Fitting to the data revealed an extremely fast decay of 62 fs. More details of the dynamics of the $3s$ Rydberg state were obtained by taking snapshots of the electron scattering distributions at different delay times. PKE distributions were also extracted from the images, but no significant changes were seen in these snapshots and PKE distributions. Hence, the $3s$ Rydberg state of 3-picoline can decay to the ground state in a time scale of 62 fs. The calculated energy of the $3s$ Rydberg state from the PKE spectrum corresponding to wavenumber 49201 cm^{-1} agrees well with the $\sim 6.1\text{ eV}$ reported by Cosmids *et al.*³⁰

4 Conclusions

Ultrafast processes arising from the optically excited states of 3-picoline were observed using femtosecond time-resolved pump-probe photoelectron imaging. By one-photon absorption at 266 nm, 3-picoline was excited to the optically bright state S_2 and the IC from S_2 state to S_1 state was observed by time-resolved PKE distributions in real time. We proposed that the secondary-populated state S_1 , excited from the S_2 state by IC, decays to the S_0 state mainly by way of IC on a time scale of 2.77 ps. The IC of the S_2 state to the highly excited S_0 state cannot be observed directly, because at our probe pulse energy, this S_0 state cannot be ionized, but appeared to be another channel. Photoelectron energy and angular distributions revealed features of ionization from the singlet $3p$ Rydberg states. The electronic wavenumbers of the $3p_1$ ($\delta=0.34$) and $3p_2$ ($\delta=0.55$) Rydberg states were determined to be 57024 and 54282 cm^{-1} , respectively. To obtain more information about the Rydberg state of 3-picoline, the $3s$ Rydberg state was populated following two-photon 400-nm excitation. The $3s$ Rydberg state of 3-picoline had probably decayed to the ground state at a time scale of 62 fs. In the context of this system, femtosecond TRPEI has proved to be a powerful tool to study ultrafast non-adiabatic dynamics.

References

- (1) Crespo-Hernandez, C. E.; Cohen, B.; Hare, P. M.; Kohle, B. *Chem. Rev.* **2004**, *104*, 1977. doi: 10.1021/cr0206770
- (2) Middleton, C. T.; Crespo-Hernandez, C. E.; Kohler, B. *Annu. Rev. Phys. Chem.* **2009**, *60*, 217. doi: 10.1146/annurev.physchem.59.032607.093719
- (3) Stolow, A.; Blanchet, V.; Zgierski, M. Z.; Seideman, T. *Nature* **1999**, *401*, 52. doi: 10.1038/43410
- (4) Schmitt, M.; Lochbrunner, S.; Shaffer, J. P.; Larsen, J. J.; Zgierski, M. Z.; Stolow, A. *J. Chem. Phys.* **2001**, *114*, 1206. doi: 10.1063/1.1331637
- (5) Suzuki, T.; Whitaker, B. J. *Int. Rev. Phys. Chem.* **2001**, *20*, 313.

- doi: 10.1080/01442350110045046
- (6) Suzuki, T.; Wang, L.; Kohguchi, H. *J. Chem. Phys.* **1999**, *111*, 4859. doi: 10.1063/1.479822
- (7) Wang, L.; Kohguchi, H.; Suzuki, T. *Faraday Discuss.* **1999**, *113*, 37. doi: 10.1039/a902866h
- (8) Tsubouchi, M.; Whitaker, B. J.; Wang, L.; Kohguchi, H.; Suzuki, T. *Phys. Rev. Lett.* **2001**, *86*, 4500. doi: 10.1103/PhysRevLett.86.4500
- (9) Matsumoto, Y.; Kim, S. K.; Suzuki, T. *J. Chem. Phys.* **2003**, *119*, 300. doi: 10.1063/1.1578062
- (10) Oku, M.; Hou, Y.; Xing, X.; Reed, B.; Xu, H.; Chang, C.; Ng, C. Y.; Nishizawa, K.; Ohshimo, K.; Suzuki, T. *J. Phys. Chem. A* **2008**, *112*, 2293. doi: 10.1021/jp0771466
- (11) Suzuki, T.; Tsubouchi, M.; Wang, L. *J. Phys. Chem. A* **2004**, *108*, 5764.
- (12) Abulimiti, B.; Zhu, R. S.; Long, J. Y.; Xu, Y. Q.; Liu, Y. Z.; Ghazal, A. Y.; Yang, M. H.; Zhang, B. *J. Chem. Phys.* **2011**, *134*, 234301. doi: 10.1063/1.3600334
- (13) Chachisvilis, M.; Zewail, A. H. *J. Phys. Chem. A* **1999**, *103*, 7408. doi: 10.1021/jp991821x
- (14) Zhong, D. P.; Diau, E. W. G.; Bernhardt, T.; Feyter, S. D.; Roberts, J. D.; Zewail, A. H. *Chem. Phys. Lett.* **1998**, *298*, 129. doi: 10.1016/S0009-2614(98)01160-9
- (15) Tsubouchi, M.; Suzuki, T. *J. Phys. Chem. A* **2003**, *107*, 10897. doi: 10.1021/jp036333a
- (16) Roebke, W. *J. Phys. Chem.* **1970**, *74*, 4198. doi: 10.1021/j100718a004
- (17) Yamazaki, I.; Baba, H. *J. Chem. Phys.* **1977**, *66*, 5826. doi: 10.1063/1.433862
- (18) Yamazaki, I.; Sushida, K.; Baba, H. *J. Chem. Phys.* **1979**, *71*, 381. doi: 10.1063/1.438081
- (19) Liu, Y. Z.; Qin, C. C.; Zhang, S.; Wang, Y. M.; Zhang, B. *Acta Phys. -Chim. Sin.* **2011**, *27*, 965. [刘玉柱, 秦朝朝, 张 嵩, 王艳梅, 张 冰. 物理化学学报, **2011**, *27*, 965.] doi: 10.3866/PKU.WHXB20110404
- (20) Long, J. Y.; Liu, Y. Z.; Qin, C. C.; Zhang, S.; Zhang, B. *Opt. Express* **2011**, *19*, 4542. doi: 10.1364/OE.19.004542
- (21) Long, J. Y.; Liu, Y. Z.; Qin, C. C.; Zhang, S.; Zhang, B. *Phys. Rev. A* **2011**, *84*, 063409. doi: 10.1103/PhysRevA.84.063409
- (22) Ding, Z. H.; Qiu, X. J.; Xu, Y. Q.; Wang, Y. M.; Zhang, B. *Acta Phys. -Chim. Sin.* **2012**, *28* (12), 2761. [丁中华, 邱学军, 徐晏琪, 王艳梅, 张 冰. 物理化学学报, **2012**, *28* (12), 2761.] doi: 10.3866/PKU.WHXB201210124
- (23) Dribinski, V.; Ossadtchi, A.; Mandelshtam, V. A.; Reisler, H. *Rev. Sci. Instrum.* **2002**, *73*, 2634. doi: 10.1063/1.1482156
- (24) Sreekanth, C. S.; Mok, C. Y.; Huang, H. H. *J. Electron Spectrosc. Relat. Phenom.* **1991**, *56*, 105. doi: 10.1016/0368-2048(91)80008-I
- (25) Suzuki, T. *Annu. Rev. Phys. Chem.* **2006**, *57*, 555. doi: 10.1146/annurev.physchem.57.032905.104601
- (26) Horio, T.; Fuji, T.; Suzuki, Y.; Suzuki, T. *J. Am. Chem. Soc.* **2009**, *131*, 10392. doi: 10.1021/ja904780b
- (27) Song, J. K.; Tsubouchi, M.; Suzuki, T. *J. Chem. Phys.* **2011**, *115*, 8810.
- (28) Cao, Z. Z.; Wei, Z. R.; Hua, L. Q.; Hu, C. J.; Zhang, S.; Zhang, B. *J. Chem. Phys.* **2009**, *130*, 144309. doi: 10.1063/1.3097184
- (29) Yang, C. N. *Phys. Rev.* **1948**, *74*, 764. doi: 10.1103/PhysRev.74.764
- (30) Kosmidis, C.; Bolovinos, A.; Tsekeris, P. *J. Mol. Spectrosc.* **1993**, *160*, 186. doi: 10.1006/jmsp.1993.1167
- (31) Lee, A. M. D.; Coe, J. D.; Ho, M. L.; Lee, S. J.; Cheng, B. M.; Zgierski, M. Z.; Chen, I. C.; Martinez, T. J.; Stolow, A. *J. Phys. Chem. A* **2007**, *111*, 11948.