

Mass-analyzed Threshold Ionization Spectrometry with Scrambling Field Optimized for the Study of State-selective Ion Reaction Dynamics[†]

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Mass-analyzed threshold ionization (MATI) technique is optimized to generate substantial amount of state-selected molecular ions sufficient for dynamics study. The main strategy is to stabilize intermediate ($n = 100$ –200) Rydberg states by lm -mixing induced by AC field. Electrical jitter inherent in high voltage switching is utilized for this purpose. A related technique to locate the MATI onset is also described.

Key Words : Mass-analyzed threshold ionization

Introduction

State selection^{1,2} of gas phase molecules is the usual starting point for the study of intramolecular and reaction dynamics,³ reaction control,^{4–6} and other manipulation of such systems. Combination of supersonic expansion⁷ and laser techniques is useful for preparation of state-selected neutrals. State selection is much more difficult for gas phase molecular ions. Conventional ionization techniques such as electron ionization and photoionization generate molecular ions with a wide distribution of quantum states.⁸ Situation is not much better with more elaborate schemes such as resonance-enhanced multiphoton ionization.⁹ Injecting ions generated by conventional means into supersonic jet often helps state selection.⁷ This technique is not generally applicable, however, due to various complications involved. Hence, one usually has to be content with energy selection rather than state selection in ionic studies using techniques such as photoelectron-photoion coincidence¹⁰ and charge exchange ionization.¹¹

Zero electron kinetic energy (ZEKE) spectroscopy¹² is a useful technique to obtain accurate thermochemical and spectroscopic information on molecular cations. In this technique, molecule is excited to a Rydberg state which lies close to the ionization threshold and ionized by electric field pulse.¹³ Lifetime of a Rydberg state gets longer as its energy approaches the ionization threshold.¹⁴ Hence, by using a long delay time (on the order of 10 μ sec) between the Rydberg state formation and pulsed field ionization (PFI), ionization can be limited to Rydberg states lying very close to the ionization threshold. An additional advantage of using a very long delay time is that electrons generated by direct ionization can be effectively eliminated during this time. Since all the rovibrational states of a cation have the

associated series of Rydberg states, a high resolution spectrum of the cation can be obtained by scanning the excitation wavelength and detecting electrons generated by PFI.

When one detects molecular ions instead of electrons in ZEKE, the technique begins to have relevance to state selection of molecular ions. Feasibility of this technique which is called mass-analyzed threshold ionization¹⁵ (MATI) was demonstrated some years ago. Currently, MATI is used as a technique complementary to ZEKE, its recognized advantage being the capability to identify the ionic species responsible for the ZEKE electron generated. Namely, its capability to generate state-selected molecular ions has not been utilized until very recently.¹⁶ As in ZEKE, molecular ions generated by direct photoionization together with Rydberg neutrals must be eliminated before pulsed field ionization of the latter in MATI. Coulomb repulsion and tiny stray electric field present in the instrument are sufficient for this purpose in ZEKE. In contrast, removal of heavy molecular ions in MATI is a more difficult task. Either a very long delay time has to be used or an extra electric field, so-called spoil field, has to be applied to separate ions generated by direct photoionization from the Rydberg neutrals. However, application of the spoil field ionizes neutrals in states very close to the ionization threshold. Exciting neutrals to Rydberg states well below the threshold is not helpful either because lifetime of a Rydberg state shortens quickly as its energy lowers. Another difficulty in MATI technique arises from the need to use high voltage switching electronics for ion acceleration in contrast with low voltage electronics used in ZEKE. Presence of stray field is unavoidable in the former. This again results in field ionization of Rydberg neutrals close to the threshold. Overall effect is the deterioration in spectral resolution and signal intensity. Overcoming these difficulties is essential for generation of state-selected ion beam with sufficient intensity for dynamics study.

In this paper, we report a method to lengthen the lifetime of Rydberg neutrals significantly and hence enhance the MATI signal intensity also by applying a weak AC field, or

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scrambling field. at the time of laser irradiation. A method to locate the MATI onset will be presented also.

Experimental Section

Nitric oxide, fluorobenzene, and cyclopentene were purchased from Aldrich and benzene from Merck and used without further purification. Nitric oxide was premixed with He in a gas reservoir while liquid samples were seeded in He carrier gas at room temperature. They were expanded into a source chamber through a nozzle orifice (0.3 mm diameter, General Valve) and skimmed through a 1 mm-diameter skimmer (Beam Dynamics) to enter a differentially pumped ionization chamber. The backing pressure was ~2 atm typically and background pressure of the ionization chamber was maintained below 10^{-7} torr.

Details of the experimental setup, Figure 1, were described previously.^{16,17} The method to generate coherent vacuum ultraviolet (VUV) radiation by four-wave difference frequency mixing¹⁸ in Kr gas is as follows. The second harmonic output of a Nd : YAG laser (Continuum PL8000, 5 ns) was used to pump a dye laser (Continuum ND6000) to generate 638 nm laser pulses. Then it was frequency-tripled to produce the 212.4 nm output (~0.5 mJ/pulse) which was used to excite the Kr $5p[1/2]_0-4p^6$ transition via two-photon resonant absorption. A laser pulse in the 500-540 nm range was also generated by a second dye laser pumped by the 355 nm output of another Nd : YAG laser. Two laser pulses were

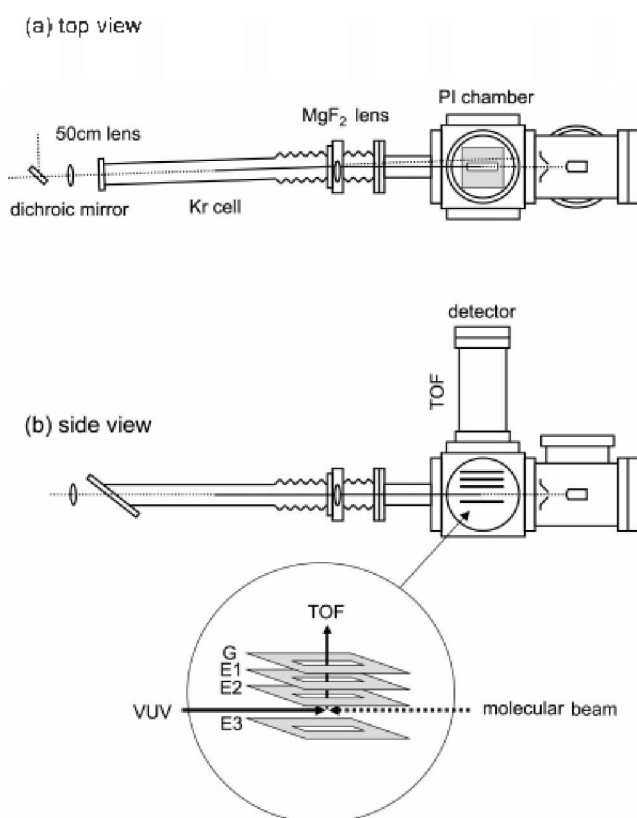


Figure 1. Schematics of VUV-MATI instrument. See text for details.

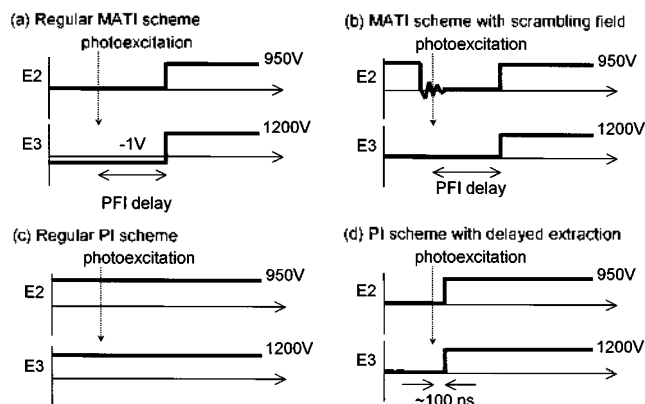


Figure 2. Voltage pulsing schemes. (a) Regular MATI scheme. (b) MATI scheme utilizing electronic jitter in high voltage switching as scrambling field. (c) Regular PI scheme. (d) PI scheme with delayed extraction. See text for details.

then combined and loosely focused by a fused-silica lens (500 mm focal length) prior to entering the Kr gas cell. A MgF_2 lens (250 mm nominal focal length) was placed off-center at the exit of the Kr gas cell to separate the VUV laser output from the input laser pulses in the laser-molecular beam interaction region.¹⁹ The VUV laser in the 132~135 nm region was generated with the Kr pressure optimized in the 1-10 torr range.

The VUV laser pulse was collinearly overlapped with the molecular beam in a counter-propagation manner to maximize the laser-molecular beam interaction volume.²⁰ Instead of the usual circular aperture, 4 mm \times 50 mm size slit electrodes were used to enhance ion collection efficiency. Figure 1. When needed, spoil field of $\sim 0.5 \text{ Vcm}^{-1}$ was applied in the ionization region to remove ions produced by direct photoionization. To achieve pulsed-field ionization (PFI) of neutrals in the high Rydberg states, an electric field of $\sim 125 \text{ Vcm}^{-1}$ was applied with the field direction perpendicular to that of the molecular and laser beams. Voltage and timing sequences are shown in Figure 2, which will be explained later. Ions generated were accelerated, flew through a field-free region, and were detected by a dual microchannel plate (MCP) detector. MATI signal detected by MCP was preamplified and A/D converted by a digital storage oscilloscope (LeCroy, LC334AM). Either the full time-of-flight mass spectrum or selected regions of the spectrum as needed were transferred to a personal computer in real time.

Results and Discussion

ZEKE states. The energies E_{nlm} of a series of Rydberg states are described by the Rydberg formula.

$$E_{nlm} = -\frac{R_M}{(n - \delta_l)^2} \quad (1)$$

Here n , l , and m are the usual quantum numbers for H-like atoms. R_M is the mass-dependent Rydberg constant ($R_\infty = 109737 \text{ cm}^{-1}$), and δ_l is the l -dependent quantum defect. A

Rydberg state with the n quantum number of 200 lies $\sim 3 \text{ cm}^{-1}$ below the corresponding series (ionization) limit.

Lifetime of a Rydberg state has been a subject of great interest.^{13,14,21-29} Extrapolation of experimental lifetimes for lower n states¹³ shows that $n \sim 200$ p-orbital Rydberg states of NO are expected to have lifetime of approximately 100 ns. Then, a much longer lifetime observed experimentally,²¹ which renders feasibility to the ZEKE and MATI techniques, is a remarkable phenomenon itself. It is generally thought that decay rate of a Rydberg state is dependent on the interaction between the Rydberg electron and the ionic core. Then, the lifetime of a Rydberg state would increase with its l quantum number because an electron in a high l orbital has small probability to be close to the ionic core. Unless built with extreme care, an apparatus tends to have a small stray field (a few tens of mVcm^{-1}).²² This stray field would cause Stark splitting of the Rydberg state prepared and l is no longer a good quantum number.^{14,23} It is generally accepted that the l mixing induced by the stray field allows transitions from the low l states to the high l states and lengthens the lifetime approximately by n .¹⁴ For a Rydberg state with $n = 200$ taken as an example above, the lifetime can become as long as 20 μs , in qualitative agreement with the experimental observations. The term ZEKE state has been coined to differentiate the high n and l states expected to be generated under the actual ZEKE experimental condition from the high n -low l Rydberg states initially prepared by photoexcitation.¹⁵

It is not that presence of electric field has only beneficial effect of lengthening the lifetime of Rydberg states. In the presence of an external field F (in Vcm^{-1}), the ionization limit of a Rydberg series is lowered from the field-free limit by

$$\Delta E (\text{cm}^{-1}) \sim 4\sqrt{F}. \quad (2)$$

For example, a stray field of 20 mVcm^{-1} lowers the ionization threshold by 0.6 cm^{-1} . Since low Rydberg states undergo rapid internal relaxation while those very close to the ionization threshold are field-ionized by the stray field, only those Rydberg states lying somewhat below the threshold, with $n = 200$ -300, will contribute to the ZEKE signal measured at 1-10 μs time delay after photoexcitation. With the presence of stronger electric field under the MATI condition, prompt ionization of high n states is unavoidable while the low n states undergo rapid internal decay. Hence, converting Rydberg states with n quantum numbers in the intermediate range, $n = 100$ -200, to the high l ZEKE states becomes a prerequisite for a successful MATI experiment.

Lifetime lengthening by scrambling field. As has been pointed out earlier, a weak DC field contributes to l mixing but does not induce any m mixing. On the other hand, inhomogeneous electric field is known to induce both l mixing and m mixing.^{14,27,28} The latter enhances the nonpenetrating character of the Rydberg orbital in high Rydberg states making the states extremely insensitive to decay processes such as autoionization, predissociation, and intramolecular relaxation. Effect of inhomogeneous field is

especially important in the absence of DC field which splits Rydberg states by Stark effect. Such an inhomogeneous electric field is produced by particles, especially charged particles, located near the Rydberg neutrals. Alternatively, inhomogeneous field can be applied intentionally in the form of a pulse or AC field. We will call it the scrambling field. General finding in such experiments is the broadening of a ZEKE peak toward the low n quantum number direction, indicating that lifetime of lower Rydberg states is lengthened due to the scrambling field. Namely, lengthening the lifetime of Rydberg neutrals in the intermediate n quantum states is not beneficial to the ZEKE spectroscopy because a wide range of Rydberg neutrals would then survive during the delay time and contribute to the PFI signal, resulting in poor spectral resolution. In MATI spectroscopy where high n Rydberg neutrals are field-ionized by spoil field, however, lengthening the lifetime of Rydberg neutrals in the intermediate n quantum states would help to maintain the PFI signal level.

Schematic drawing of the electrode assembly used in this work to study the effect of scrambling field on the lifetime of Rydberg neutrals is shown in Figure 1. The assembly consists of three electrodes E_1 , E_2 , and E_3 , of which E_1 is the ground electrode. Usual pulsing scheme, or scheme I, is shown in Figure 2(a). Small DC voltage on the E_3 electrode provides the spoil field needed to remove direct ions. After some time delay, high voltages are applied on the E_2 and E_3 electrodes for pulsed field ionization of Rydberg neutrals and acceleration of MATI ions thus generated. High voltages on both electrodes are needed for mass-independent time focusing of MATI signals. Unlike in ZEKE where only low voltage pulses are needed, high voltage switching needed in MATI makes it difficult to apply scrambling field between the E_2 and E_3 electrodes. One may give up time focusing and pulses the E_3 voltage while the E_2 electrode is used for application of the scrambling field. Then, the result is a very poor mass spectral resolution for MATI signals. To avoid the above difficulties, we devised a new scheme which utilizes the ringing, or jitter, present when a high voltage is switched off. In the scheme shown in Figure 2(b), or scheme II, the high voltage on the E_2 electrode is switched off just before laser irradiation. The voltage ringing with the frequency of $\sim 100 \text{ MHz}$ provides the scrambling field. With the scrambling field on, direct ions are removed more rapidly than in the absence of this field. We attribute this to the DC component of scrambling field, which serves as the spoil field. By comparing with the measured disappearance rate of direct ions in the presence of externally applied spoil field, we estimate that the DC component of scrambling field is $\sim 0.3 \text{ Vcm}^{-1}$. Namely, the voltage ringing serves dual purposes of providing scrambling and spoil fields. Additional spoil field can be applied also in this scheme but is usually not needed.

MATI experiment was performed for NO with schemes I and II. PFI delay time was varied to observe the effective lifetime of Rydberg neutrals. Time-dependent decays of MATI signals obtained with schemes I and II are shown in Figures 3(a) and 3(b), respectively. It is to be noted that most of the MATI signal decays rapidly, within $\sim 100 \text{ nsec}$, in

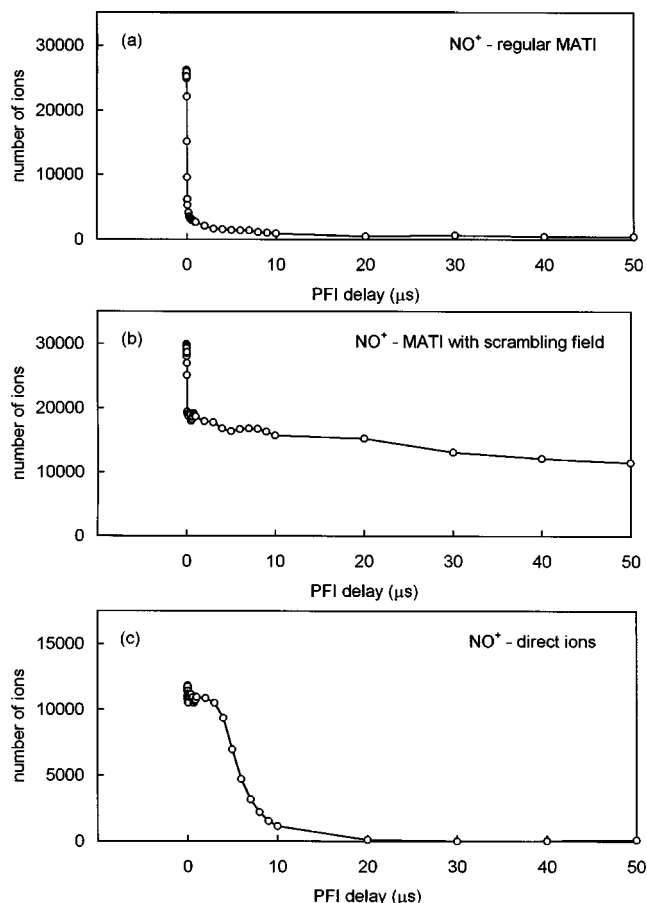


Figure 3. Ion yield as a function of delay time between photoexcitation and pulsed field ionization of NO. (a) Regular MATI. (b) MATI with scrambling field. (c) Ions generated by direct photoionization.

scheme I. Even though similar rapid decay is observed in scheme II also, around 40% of the signal persists even after 50 μsec time delay. Also shown in the figure. Figure 3(c), is the time dependent decay of the direct ion signal obtained with scheme II with a laser wavelength where MATI signal was absent. It takes around 20 μsec to remove the direct ions completely. Then, by using delay time longer than 20 μsec , a high resolution time-of-flight MATI spectrum with high intensity can be obtained which is free from direct ion contamination. Similar experiments have been done for benzene. Figure 4. Here again, lifetime enhancement by the scrambling field is apparent. We have carried out similar experiments for many other systems and observed comparable results. We could generate more than 500 state-selected molecular ions per laser pulse, which was sufficient for dynamics study.

Determination of the MATI threshold. As has been mentioned so far, the main difficulty in generating substantial amount of state-selected molecular ions by MATI is associated with the removal of direct ions and with the use of high voltage switching electronics. Our new scheme avoids this difficulty by lengthening the lifetime of lower-lying ($n = 100\text{--}200$) Rydberg states utilizing high voltage jitter. Then, the energy levels of the Rydberg states sampled are quite

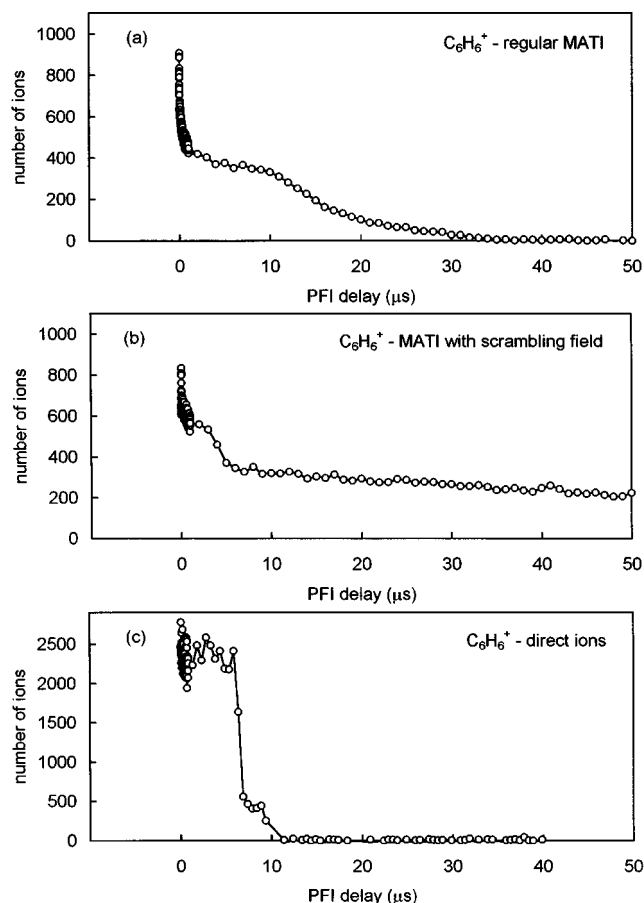


Figure 4. Ion yield as a function of delay time between photoexcitation and pulsed field ionization of benzene. (a) Regular MATI. (b) MATI with scrambling field. (c) Ions generated by direct photoionization.

below the ionization threshold. Searching for a MATI peak, usually the 0-0 peak, becomes a practical difficulty in this scheme, which requires substantial amount of time and effort.

A simple method to find the MATI onset, or the 0-0 peak position, is to record the photoionization efficiency (PIE) curve, or the intensity of the direct ion current as a function of the photon energy. In the usual scheme to record the PIE curve, high DC voltages are applied to the electrodes E_2 and E_3 to extract direct ions generated by photoionization between these electrodes, Figure 2(c). The PIE curve of benzene thus obtained is compared with the 0-0 MATI peak position in Figure 5(a). It is to be noted that the PI threshold lies substantially below the MATI onset and is not helpful in locating the latter. There are two reasons for lowering of the PI threshold. First, due to the presence of high electric field in the ionization region, the ionization thresholds of lower-lying Rydberg states are lowered. Or, the Rydberg states lying well below the ionization threshold are field-ionized under this condition. Second is the ionization due to hot band transition, whose contribution varies with the experimental condition such as the molecular beam expansion condition. To avoid the first difficulty, we attempted a switching

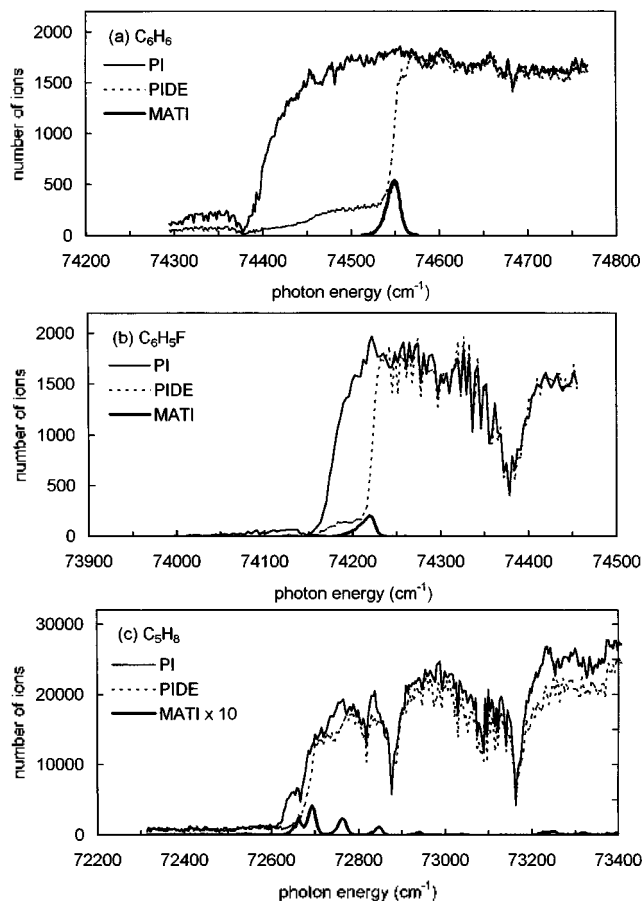


Figure 5. Photoionization efficiency curves obtained under regular (PI) and delayed extraction (PIDE) conditions are compared with MATI spectra for (a) benzene, (b) fluorobenzene, and (c) cyclopentene.

scheme for extraction of the direct ions. In this scheme, which will be called photoionization with delayed extraction (PIDE), photoionization is carried out under the field-free condition. Then, after ~ 100 ns time delay, the accelerating field is switched on, Figure 2(d). PIE curve of benzene obtained with the PIDE technique is shown in Figure 5(a) also. It is to be noted that the PIE curve recorded with PIDE is shifted toward higher energy compared to the one recorded under the DC condition. It is because the lower-lying Rydberg neutrals decayed during the 100 nsec delay and did not undergo field-ionization anymore when high electric field was switched on. Even though photoionization by hot band transition also appears under the delayed extraction, the correct ionization threshold can be easily identified. More importantly, the figure shows that the PI threshold under the delayed extraction condition nearly coincides with the MATI onset. Namely, by recording PIE curve under the delayed extraction condition, the MATI onset can be readily located. We performed similar experiments for various molecules and observed good coincidence between the PIDE and MATI onsets. The results for fluorobenzene and cyclopentene are shown in Figures 5(b) and 5(c), respectively, as examples. It is to be noted that the mismatch between the regular PI and MATI onsets differs

for different systems and also for different experimental conditions. Regardless, the MATI onset is always coincident with the PI onset observed under the delayed extraction condition.

Conclusion

Electronic jitter appearing when a high voltage is switched off has been utilized as a means to apply AC field, or scrambling field, to high Rydberg neutrals generated by resonant VUV excitation. It has been found that strong MATI signal persists after PFI delay time as long as 50 μ sec. It is thought that the lifetime of Rydberg neutrals somewhat below the ionization threshold, $n = 100$ -200, has been lengthened through the l - m -mixing induced by scrambling field. Most importantly, the intensity of the state-selected molecular ion beam generated by MATI has increased tremendously with the use of scrambling field. Now the technique seems to be adequate for the study of state-selective ion reaction dynamics.

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