J. Synchrotron Rad. (1997). **4**, 6–13

Development of a Tunable UV Laser System Synchronizing Precisely with Synchrotron Radiation Pulses from UVSOR

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(*Received 17 July 1996; accepted 29 October 1996*)

A mode-locked Ti:sapphire laser is made to oscillate at the frequency of the UVSOR storage ring, 90.115 MHz, in a multi-bunch operation mode. The third harmonic of the laser is available in the wavelength range 243–280 nm. Synchrotron radiation from an undulator is monochromatized by a grazing-incidence monochromator and introduced coaxially with the laser. The temporal profile of the photon pulses is monitored *in situ* by a luminescing substance/photomultiplier combination. The delay timing between the laser and synchrotron radiation can be changed from 0 to 11 ns by adjusting an electronic module that provides phase-locked loop stabilization of the laser pulse. The reliability and feasibility of this laser–synchrotron radiation combination technique are demonstrated by applying pump-probe experiments to two physical systems. The first system is photodissociation of iodomethane (CH_3I) with a laser photon, followed by photoionization of I and CH_3 fragments with synchrotron radiation. The second, two-photon ionization of He atoms, is studied as the prototype of a time-resolved experiment. The He^+ signal counts as a function of the laser–synchrotron radiation delay are found to be enhanced in a narrow time window, which can be interpreted in terms of a short lifetime of the resonant state, $He^*(1s2p\ ^1P)$, produced by primary synchrotron radiation excitation.

Keywords: laser–synchrotron radiation combination; mode-locked lasers; pump-probe experiments; UVSOR; photodissociation; two-photon ionization.

1. Introduction

Combining the laser with synchrotron radiation has attracted widespread attention from molecular scientists whose main interests are in phenomena induced by electronic transitions. Synchrotron radiation is characterized by its extremely wide wavelength coverage from the far IR to the hard X-ray region. In contrast, lasers are superior to synchrotron radiation in the UV and visible regions because they provide a photon flux of five to ten orders of magnitude higher than synchrotron radiation. Recent rapid progress in laser technology has led to great improvements in energy ranges and spectral and/or temporal resolution. By making the most of these different features of the two photon sources, one can expect various types of pump-probe or double-resonance experiments for investigating the spectroscopy and dynamics of a particular vibronic state in detail. Since the pioneering work on highly excited alkali-metal atoms produced by two-photon excitation (Bizau *et al.*, 1985; Meyer *et al.*, 1987), numerous papers have been published over the last ten years dealing with direct photoionization of inner-shell electrons of laser-excited atoms and resonant excitation of laser-excited and aligned atoms followed by autoionization (Dohrmann & Sonntag, 1996). In contrast, studies invoking the laser–synchrotron radiation combination have been restricted to very few molecular systems: photoelectron spectroscopy of atomic iodine produced from I_2 (Nahon *et al.*, 1990; Nahon, Svensson & Morin, 1991), and photoelectron spectroscopy of N_2 and HCN produced by laser photodissociation of *s*-tetrazine (Nahon, Morin, Larzillière & Nenner, 1992).

Very recently, time-resolved spectroscopy in the gas phase has been achieved by means of a mode-locked Ar-ion laser synchronized with the radiation emitted from the Super ACO storage ring (Lacoursière, Meyer, Nahon, Morin & Larzillière, 1994; Meyer *et al.*, 1996). They succeeded in synchronizing every ninth laser pulse with a synchrotron radiation pulse at a repetition rate of 8.32 MHz. This frequency corresponded to the two-bunch operation of the storage ring. The wavelength of the Ar-ion laser was fixed at 514.5 nm. A similar time-resolved experiment has been performed by Gatzke *et al.* (1995) using a mode-locked Ti:sapphire laser synchronized with the undulator radiation emitted from the BESSY storage ring. They used synchrotron radiation in the single-bunch operation mode at a repetition rate of 4.8 MHz. Undoubtedly, the results of these groups represented a significant breakthrough in many related fields in molecular science, but there still remain several problems that should be solved before the

laser–synchrotron radiation combination technique is put to practical use. It has often been documented that the principal difficulty in fulfilling a time-resolved pump-probe experiment using the laser–synchrotron radiation combination is the limitation of the photon energy range of available lasers. Previous experiments were performed using the visible light from an Ar-ion laser (Lacoursière *et al.*, 1994; Meyer *et al.*, 1996), a frequency-doubled Ti:sapphire laser (Gatzke *et al.*, 1995), or a frequency-doubled Nd:YAG laser (Mitani *et al.*, 1989; Ederer *et al.*, 1992). The shorter-wavelength region has not been approached owing to the lack of appropriate UV lasers that oscillate at a high repetition rate compatible with the frequency of the electron storage ring of an ordinary synchrotron radiation facility. A tunable UV laser is indispensable in producing an electronically excited state of small molecules if one wishes to probe the dynamical behaviour of the excited state with a time-correlated synchrotron radiation photon pulse. Now, the above barrier is being overcome by the development of solid-state mode-locked lasers, in particular, by a technical innovation of Ti:sapphire lasers.

This paper describes a novel laser–synchrotron radiation combination system in which precise synchronization of the photon pulses has been realized between the third harmonic of a Ti:sapphire laser and the undulator radiation emitted from the UVSOR storage ring in Okazaki. We have taken maximum advantage of the up-to-date Ti:sapphire laser. Its oscillation at a high frequency permits a photon pulse of the laser to be synchronized with that of synchrotron radiation in the multi-bunch operation mode. Furthermore, its wide tunability in the UV region contributes towards our wide selection of target molecules. The main purpose of this paper is to describe technical aspects of laser–synchrotron radiation synchronization, including experimental set-up and basic performance. We also give two examples of applications to real physical systems.

2. Experimental set-up

2.1. *General features*

Fig. 1 shows a schematic diagram of the apparatus for laser–synchrotron radiation synchronization experiments. A mode-locked Ti:sapphire laser is made to operate synchronously with a master oscillator (90.115 MHz) for a main radio-frequency cavity on the UVSOR storage ring. The third harmonic of the laser is introduced coaxially into a photoionization vacuum chamber, with the fundamental of the undulator light supplied from beamline BL3A2. The sample gas is expanded from a nozzle made of a multi-channel capillary array plate (Hamamatsu, J5022-01, 12 μm channel diameter). The molecular beam intersects the two photon beams at 90° at a cylindrical ionization cell. Photoions are analyzed by a quadrupole mass filter (Extrel, 041-12 and 7-162-8) placed perpendicular to the photon beams and the molecular beam. The acceleration energy for ions entering the quadrupole ranges from 10 to 15 eV. The ambient pressure in the vacuum chamber is monitored by an ionization gauge and kept constant at 3×10^{-6} or 7×10^{-6} Torr when the neat sample of CH_3I or He, respectively, is introduced.

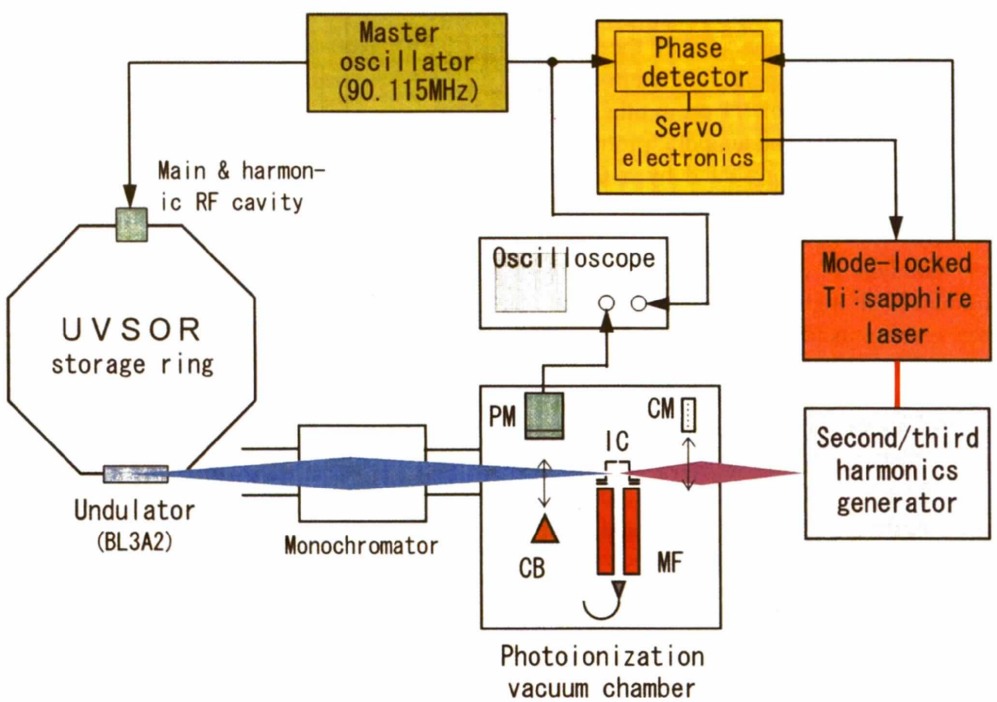

Figure 1
Schematic diagram of the apparatus for the laser–synchrotron radiation synchronization experiment. PM, photomultiplier; CM, gold-mesh current monitor; IC, ionization cell; CB, Cu block; MF, quadrupole mass filter.

2.2. *Mode-locked laser*

The repetition rate of the mode-locked Ti:sapphire laser (Spectra Physics Lasers, Tsunami, 3950-L2S) has been changed from 82 MHz (standard version) to 90.115 MHz to match the frequency of the UVSOR storage ring. The pumping source is an Ar-ion laser of 8.5–10 W operated on all lines (Spectra Physics Lasers, BeamLok, 2060-10SA) with a 'silent light' option. The Ti:sapphire laser produces photon pulses with a duration of ~ 1.8 ps. An acousto-optic modulator placed in the laser intracavity is used to maintain stable long-term operation of the self-mode-locked laser. The second and third harmonics are generated by using a lithium triborate crystal (Spectra Physics Lasers, frequency doubler, 3980-1S) and a β-barium borate crystal (Spectra Physics Lasers, frequency tripler, GWU-3), respectively. In normal operation, the typical output power of the laser is 1.2 W, 200 mW and 50 mW for the fundamental (780 nm), the second harmonic (390 nm) and the third harmonic (260 nm), respectively. The pulse energy of the third harmonic is 0.6 nJ at 250–270 nm (8×10^8 photons pulse^{-1}), and decreases down to 0.2 nJ at 245 or 275 nm. The third harmonic is separated with dichroic mirrors and focused using a fused-silica spherical plano-convex lens (focal length ~ 500 mm) onto the centre of the ionization cell.

2.3. *Synchrotron radiation*

Beamline BL3A2 has been developed in order to use intense quasi-monochromatic radiation emitted from a planar-type undulator installed in a long straight section of the storage ring (Yonehara *et al.*, 1985). The undulator possesses 24 periods, each of which is 80 mm in length. All test experiments described in §3 are performed by using the fundamental light, $U1$. Fig. 2 shows the dependence of the photon energy of $U1$ on the gap of the inserted magnets. Here, E_{SR}^{max} denotes the peak maximum position in the intensity distribution curve of $U1$ or, in other words, the centre of the spectral profile. The temporal profile of the synchrotron radiation pulse is represented by a Gaussian function with a full width at half maximum (FWHM) of approximately 400 ps.

The undulator radiation is reflected by a prefocusing mirror and introduced through an entrance slit into a constant-deviation grazing-incidence monochromator with a 2.2 m focal length (Ishiguro *et al.*, 1989). The monochromator covers a wide wavelength region of ~ 10–100 nm by interchanging three gratings, $G1$ (600 lines mm^{-1}) at 95.3–22.5 nm, $G2$ (1200 lines mm^{-1}) at 53.8–12.4 nm, and $G3$ (2400 lines mm^{-1}) at 27–9.9 nm. The directions of the incidence and monochromatized lights are fixed and parallel to each other because a plane mirror located between the grating and an exit slit reflects back the first-order light of the grating. The wavelength-scanning mechanism involves rotation of the grating, together with translation of the grating and the plane mirror along the direction of the incident light. A vacuum chamber containing the grating and the plane mirror is connected to the fixed entrance and exit slits with bellows and moves on a bed inclined at 14°.

The monochromatized synchrotron radiation is focused by a post-focusing mirror onto the ionization region. The pump-probe CH_3I experiment in §3.2 is carried out with the position of $G1$ set at the zeroth-order light. In this case a lithium fluoride (LiF) window is placed upstream of the ionization cell to prevent the second and higher harmonics of the undulator light from entering the cell. For the time-resolved spectroscopy of He*($1s2p$ ^1P) in §3.3, the first-order light of $G1$ is chosen within the undulator bandwidth. The average photon flux is measured with a movable current monitor made of gold mesh, which is installed downstream of the ionization cell.

The stability of the electron beam in the storage ring has been greatly improved by employing a third-harmonic radio-frequency cavity because the longitudinal coupled-bunch instability can be suppressed by introducing Landau damping (Hama, 1996). The jitter between two consecutive electron bunches is estimated to be less than 10 ps by using the dual-sweep streak camera technique.

2.4. *Detector of the photon pulse*

Detection of photon pulses *in situ* using a high-bandwidth photosensitive device is essential for attaining precise synchronization between the laser light and synchrotron radiation. For this purpose we monitor fluorescence at ~ 340 nm from *p*-terphenyl ($C_{18}H_{14}$) excited by the laser (Lambda Physik GmbH, 1986) and Auger-free luminescence at ~ 220 nm from BaF_2 excited by the undulator radiation (Itoh, Hashimoto, Sakuragi & Kubota,

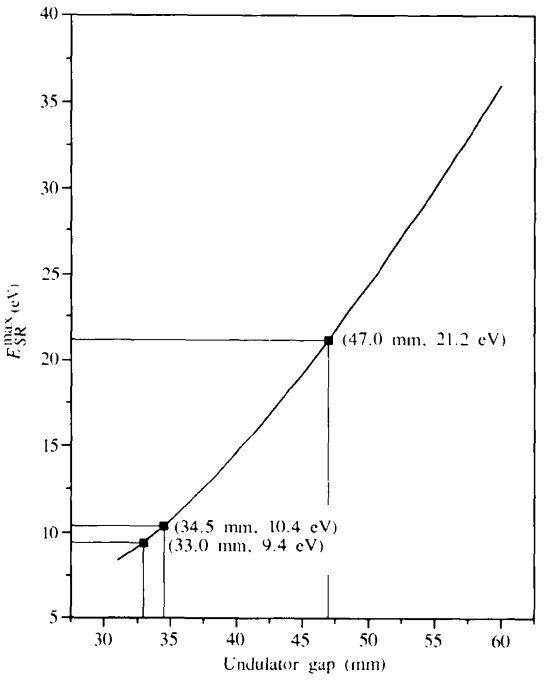

Figure 2
Photon energy of the fundamental of the undulator radiation supplied from beamline BL3A2 as a function of the gap of the inserted magnets. The ordinate represents the peak maximum position in the intensity distribution curve of the radiation or, in other words, the centre of the spectral profile.

1988). The observed lifetimes of the fluorescence from the two compounds are of the same order (900 ps). Both lights are simultaneously detected with a metal package photomultiplier tube (Hamamatsu, R5600U-06). A Cu block, having a triangular prism shape, is inserted across the photon beam axis at a point 44 mm from the centre of the ionization cell, as shown in Fig. 3. The laser light impinges on one of the rectangular sides covered by a thick film of *p*-terphenyl with an incident angle of 45°, while a piece of BaF_2 crystal glued on the other side is illuminated by the undulator radiation. To examine the temporal and spatial overlap, the output current of the photomultiplier is amplified by a preamplifier (ORTEC, VT120A) and fed into a digital oscilloscope (Iwatsu-LeCroy, 9362, 1.5 gigasamples s^{-1}). The Cu block is connected to the rod of a linear-motion feedthrough so it can be easily put in and out of the path of the photon beams without breaking the system vacuum.

3. Experimental results and discussion

3.1. *Adjusting the timing between the laser and synchrotron radiation*

Synchronization of the laser to the undulator radiation is performed by use of an electronics module which provides phase-locked loop stabilization of the laser pulse (Spectra Physics Lasers, Lok-to-Clock, 3930). A small fraction of the laser output is monitored on a photodiode placed near the output coupler of the laser (not explicitly drawn in Fig. 1). The phase of the train of the laser output pulse is compared with that of the reference signal, the 90.115 MHz synchronous output from the master oscillator of the UVSOR storage ring. Any phase difference is converted into an error voltage by a phase detector, which is used to drive a piezo-electric transducer mounted on one of the intracavity mirrors in the Ti:sapphire laser. This changes the cavity length of the laser and consequently the pulse repetition frequency. When the timing is perfect between the laser output pulses and the reference signal, the cavity length is held constant to maintain synchronization. The nominal timing jitter of the 'lok-to-clock' electronics has been evaluated to be less than 3 ps by measuring the cross-correlation signal for two mode-locked Ti:sapphire lasers, as described in the *User's Manual* provided by Spectra Physics Lasers (1994).

We can adjust the temporal overlap of the photon pulses between the laser and synchrotron radiation using a DC-voltage-controlled phase shifter in the 'lok-to-clock' electronics by monitoring the output of the photomultiplier on a trace of the digital oscilloscope. Fig. 4 shows the traces of the photomultiplier signal for two different cases of the timing. The reference signal from the master oscillator is supplied to the trigger input of the oscilloscope. If the timing of the photon pulses between the laser and synchrotron radiation is different, two pulse trains with the same interval of 11 ns are observed in separate positions, as indicated in Fig. 4(*a*). Here, the synchrotron radiation pulse arrives at the Cu block 3.4 ns earlier than the laser pulse.

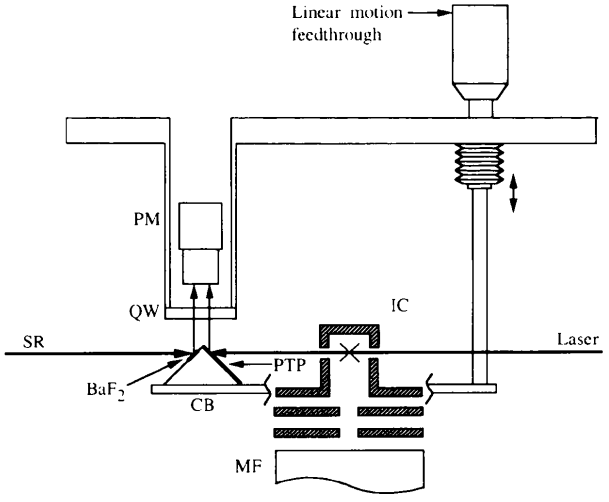

Figure 3
Schematic diagram of the detector of the photon pulse. The luminescence emitted from the surface of a Cu block (CB) passes through a vacuum-sealed quartz window (QW) and is admitted to a photomultiplier tube (PM). The adopted luminescing substances are *p*-terphenyl (PTP) and BaF_2 for the laser and synchrotron radiation, respectively. All materials except for an ionization cell (IC) and a quadrupole mass filter (MF) are mounted on a vacuum flange of diameter 8".

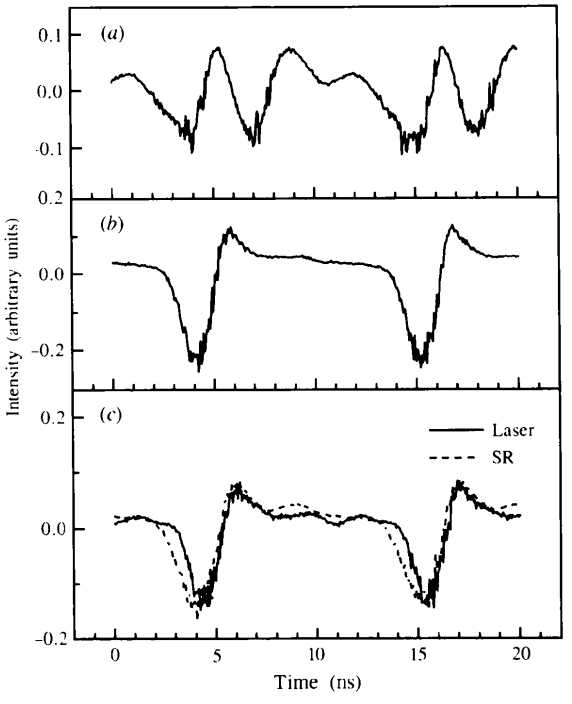

Figure 4
Traces of the photomultiplier signal on a digital oscilloscope for two different cases of the timing between the laser and synchrotron radiation. The delay of the laser pulse at the Cu block with respect to the synchrotron radiation pulse is 3.4 ns in (*a*) and 0.3 ns in (*b*) and (*c*). At the 0.3 ns delay, the two photon pulses are considered to be definitely overlapped in time at the ionization cell. They are monitored either simultaneously in (*a*) and (*b*) or individually in (*c*).

In Fig. 4(*b*) the phase shifter is adjusted so that the two pulse trains are almost overlapped in time. A precise value of the delay can be estimated to be 0.3 ns from Fig. 4(*c*), in which the laser and synchrotron radiation pulses are individually recorded by blocking the two photon beams alternately. This 0.3 ns delay at the Cu block corresponds to a delay of (0 ± 0.1) ns at the centre of the ionization cell, which is 44 mm from the block. Thus, the pulses of the laser and synchrotron radiation are expected to be definitely overlapped in time at the ionization region.

Viewing the signal on the oscilloscope permits the delay time between the laser and synchrotron radiation pulses to be measured with a precision of ±100 ps. The whole system operates stably at a fixed delay within this resolution limit for 2–3 h without readjustment of the timing.

3.2. *Pump-probe experiment of CH_3I*

The performance of the whole experimental set-up has been examined by means of tests on real physical systems. First, sequential absorption of the two different photons requires a good spatial overlap of the photon pulses between the laser and synchrotron radiation. In order to inspect the practical conditions, we make use of synchrotron radiation photoionization of the fragments produced by laser photodissociation of CH_3I. The high photon flux of the third harmonic of the laser permits a non-bonding valence electron to be excited to an antibonding orbital. The excited state thus formed undergoes rapid dissociation into neutral fragments. If spatial overlap of the laser and synchrotron radiation is sufficient, it is expected that the fragments will be further ionized by an undulator photon.

The scheme of the pump-probe experiment is expressed as

$$CH_3I + h\nu_1 (E_{laser} = 4.79\,eV) \rightarrow CH_3(\tilde{X}^2A_2'') + I(^2P_{1/2}, {}^2P_{3/2}), \quad (1)$$

$$I(^2P_{1/2}, {}^2P_{3/2}) + h\nu_2 (E_{SR}^{max} = 9.4\,eV) \rightarrow I^+ + e\,, \quad (2)$$

$$CH_3(\tilde{X}^2A_2'') + h\nu_2 (E_{SR}^{max} = 10.4\,eV) \rightarrow CH_3^+(\tilde{X}^1A_1') + e\,. \quad (3)$$

In process (1), irradiation of the third harmonic of the laser at 259 nm results in dissociation of CH_3I into an I atom and a methyl radical (Okabe, 1978; Chandler & Houston, 1987). The two fragments are subsequently ionized in processes (2) and (3) with the *U*1 light, whose spectral profile is centred at E_{SR}^{max} = 9.4 and 10.4 eV, respectively. In order to obtain maximum photon flux, we directly introduce the zeroth-order light of *G*1 into the ionization region. The energy spread of *U*1 is estimated to be no less than 0.5 eV (FWHM). A typical electric current measured at the gold-mesh monitor is 20–40 nA, which corresponds to a synchrotron radiation photon flux of (0.8–1.6) × 10^{13} photons s^{-1}. When E_{SR}^{max} is set at 9.4 eV, at most half of the photons in the undulator bandwidth can be used to ionize the iodine fragment, since the ionization potentials of the two fine structures $I(^2P_{1/2})$ and $I(^2P_{3/2})$ are 9.51 and 10.45 eV, respectively. Nevertheless, we chose this value of E_{SR}^{max} to realize the condition that $I(^2P_{1/2})$ is allowed to be ionized but $I(^2P_{3/2})$ is not.

The advantage of the present laser–synchrotron radiation combination experiment is that the cut-off energy of LiF (~ 12 eV) lies above the ionization potential of every fragment [see the above values for $I(^2P_{1/2}, {}^2P_{3/2})$ and 9.84 eV for CH_3]. In contrast, the dissociation limits of CH_3I are 12.86 and 12.25 eV for the formation of $I^+ + CH_3$ and $I(^2P_{3/2}) + CH_3^+$, respectively. From these energetic relations, an LiF window located upstream of the ionization cell is found to be very effective in excluding the second and higher harmonics which would otherwise bring about a significant background of I^+ or CH_3^+ produced by dissociative photoionization of CH_3I. Such a background should be kept as low as possible to obtain good reproducibility of the pump-probe signal. Actually, the signal-to-background ratio is enormously improved by using the LiF window.

Fig. 5 shows the mass spectra of ions produced by synchrotron radiation photoionization with and without the 4.79 eV laser light in the *m*/*z* range 125–131. The mass resolution, $m/\Delta m$, is estimated to be *ca* 70. When the laser is introduced with the synchrotron radiation, the I^+-ion count shows a marked increase at *m*/*z* 127, which provides conclusive evidence for sequential absorption of

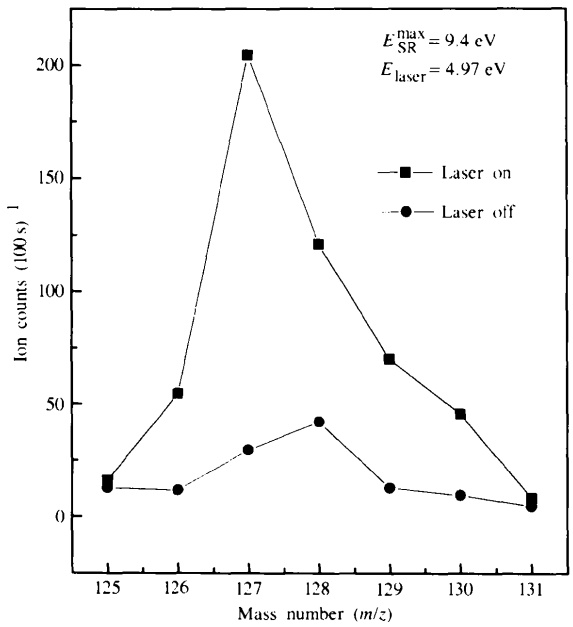

Figure 5
Mass spectra of the ions produced from CH_3I in the pump-probe experiment. The mass resolution is set to $m/\Delta m \simeq 70$. The undulator light, the spectral profile of which is centred at E_{SR}^{max} = 9.4 eV with a FWHM of ~0.5 eV, is directly introduced without being monochromatized. The two curves represent mass spectra with the laser on and off. A pronounced peak at *m*/*z* 127 is ascribed to the I^+-ion counts resulting from laser photodissociation of CH_3I followed by photoionization of iodine fragments with the undulator radiation. A small peak at *m*/*z* 128 with the laser off might result from single-photon ionization of hydrogen iodide (HI), an impurity in the sample, or residual hydrocarbons in the vacuum chamber.

the two different photons. Typical count rates of the pump-probe signal and background are 2 and 0.2 counts s^{-1}, respectively. Similarly, the laser irradiation is found to augment the ion counts of CH_3^+ (m/z 15) at E_{SR}^{max} = 10.4 eV. There is no dependence of the signal counts on the delay of the photon pulses between the laser and synchrotron radiation. This can be explained by the interval time of synchrotron radiation (11.097 ns) being much shorter than the residence time of the fragments in the ionization region: 800–1000 and 110–130 ns for I and CH_3, respectively. These values are evaluated from the reported kinetic energy release in process (1) (Barry & Gorry, 1984; Riley & Wilson, 1972).

The pump-probe signal detected in Fig. 5 is mainly ascribed to the synchrotron radiation ionization of $I(^2P_{1/2})$ preceded by the laser photodissociation of CH_3I for the following two reasons. First, the ionization potential of $I(^2P_{3/2})$, 10.45 eV, is much greater than the photon energies within the undulator bandwidth of 0.5 eV when E_{SR}^{max} is set at 9.4 eV. Second, the branching ratio of the iodine fragment between $I(^2P_{3/2})$ and $I(^2P_{1/2})$ is reported to be 22 and 78% in the study of laser photodissociation at 266 nm (Riley & Wilson, 1972).

When E_{SR}^{max} is increased to 10.4 eV the signal-to-background ratio for the pump-probe signal of I^+ becomes small on account of significant overlapping of ion counts around m/z 128, which appears independently of the introduction of the laser. It is likely that HI^+ ions are produced by synchrotron radiation photoionization of HI contained in the sample as an impurity. The count rate of the m/z 128 background is much higher at E_{SR}^{max} = 10.4 eV than at 9.4 eV. This can be explained by the fact that the first ionization potential of HI is 10.38 eV.

3.3. *Time-resolved spectroscopy of He*(1s2p ^1P)*

Time-resolved spectroscopy of isolated atoms or molecules should be carried out to obtain direct evidence supporting the precise synchronization between the laser and synchrotron radiation, and to check the performance of the adjustment mechanism for pulse timing. A method quite pertinent to this purpose is multiphoton ionization using the laser–synchrotron radiation combination; namely, a short-lived excited state is produced by synchrotron radiation photoexcitation and its lifetime is measured by means of laser photoionization mass spectrometry. Extensive experimental and theoretical studies have been made on multiphoton ionization using one-colour or two-colour laser techniques, which are summarized in several comprehensive review articles (Tanaka & Kawasaki, 1984; Ito & Fujii, 1988). Nevertheless, multiphoton ionization studies using the laser–synchrotron radiation combination have been restricted so far to three physical systems: laser photoelectron spectroscopy of He*($1s3p$ ^1P) produced by synchrotron radiation excitation at 23.09 eV (Lacoursière *et al.*, 1994; Meyer *et al.*, 1996), laser photoionization mass spectrometry of Xe*($5p^5 5d$ $[3/2]_1$) produced by synchrotron radiation excitation at 10.40 eV (Meyer *et al.*, 1996), and synchrotron radiation photoelectron spectroscopy of Ca*($4s4p$ $^1P_1$) produced by laser excitation at 2.93 eV (Gatzke *et al.*, 1995). In all cases, pulse timing of synchrotron radiation was made to synchronize precisely with that of a mode-locked laser and the overall temporal resolution was estimated to be ~1 ns.

In the present study we chose the He*($1s2p$ ^1P) state which has a radiative lifetime of approximately 0.555 ns (Radzig & Smirnov, 1985). The scheme of the two-photon ionization is expressed as

$$\mathrm{He} + h\nu_1 (E_{SR} = 21.218\ \mathrm{eV}) \rightarrow \mathrm{He}^*(1s2p\ ^1P), \quad (4)$$

$$\mathrm{He}^*(1s2p\ ^1P) + h\nu_2 (E_{laser} \simeq 4.8\ \mathrm{eV}) \rightarrow \mathrm{He}^+ + \mathrm{e}^-. \quad (5)$$

The primary excitation with the $U1$ light produces a resonant state He*($1s2p$ ^1P). After a specific lapse of time the excited atom is photoionized by absorbing another photon, the third harmonic of the laser at ~260 nm. Consequently, the ion counts measured as a function of the delay between the laser and synchrotron radiation exhibit a decay curve associated with the lifetime of He*($1s2p$ ^1P). The overall temporal resolution is determined theoretically from the temporal profile of the synchrotron radiation pulse, *i.e.* the FWHM of 400 ps.

For process (4), $U1$ at the 47 mm gap is monochromatized by grating $G1$. The spectral resolution of the first-order light is estimated to be ~15 meV (FWHM) by measuring the ion counts of He^+ produced in process (5) as a function of the photon energy. Two 100 nm-thick Sb foils are prerequisite to suppressing the second- and higher-order lights from $G1$ which produce serious He^+ background noise resulting from single-photon ionization. An optical chopper (Stanford Research Systems, SR540) modulating the laser beam with a 50% duty ratio is used to alternate the data-acquisition cycle of the laser on and off at 100 Hz in combination with a dual-channel gated photon counter (Stanford Research Systems, SR400). Thereby, we were able to compensate for the transient changes or long-term drifts in the experimental conditions, such as a monotonic decrease in the synchrotron radiation photon flux and the variation of the sample pressure. If the on and off cycle were much longer, the changes and drifts would severely reduce the reliability of the data on account of a small signal-to-background ratio (less than 0.2).

A typical electric current measured at the gold-mesh monitor is 5 pA, which corresponds to a synchrotron radiation photon flux of 2.0×10^9 photons s^{-1}. The size of the synchrotron radiation photon beam is *ca* 1×1 mm^2 inside the ionization cell. We can therefore estimate that ~0.04% of ground-state He atoms are excited to He*($1s2p$ ^1P) per second in process (4). In this estimate the oscillator strength of 0.276 is taken from the literature (Radzig & Smirnov, 1985) and 1% of the photon flux is considered to be efficient for the transition because of a narrow Doppler width (< 0.15 meV) as compared with the spectral resolution of synchrotron radiation. The count rate of the He^+ signal is then estimated to be 0.3 counts s^{-1} by multiplying 0.04%

by the He number density of 3.3×10^{11} atoms cm^{-3} (at 10^{-5} Torr), the laser intensity of 9×10^{18} photons s^{-1} cm^{-2} (at 70 mW), the ionization volume of 2×10^{-3} cm^{-3}, the reciprocal of the repetition rate of 90.115 MHz, and the ionization cross section, σ_{ion}, of He*($1s2p$ ^1P) at 4.8 eV. Here, σ_{ion} is assumed to be 1×10^{-17} cm^2, and the pulses of the laser and synchrotron radiation are expected to be precisely overlapped in time at the ionization region.

Fig. 6 shows the ratio between the He^+ signal counts, with and without the laser, as a function of the delay of the laser pulse with respect to the synchrotron radiation pulse. At 1 ns or longer delays the ratio is almost constant at 0.95, though the data points show some scatter. Accordingly, we assume that this value corresponds to the background level. Its deviation from unity probably arises from the uncertainty with regard to the effective gate time of the gated photon counter operating with the optical chopper. The ratio in Fig. 6 is found to be greater than the background level within a narrow time window from −100 to +400 ps. This enhancement can be accounted for by the He^+ signal counts due to the two-photon ionization by way of He*($1s2p$ ^1P). The count rate of the pump-probe signal is 0.2–0.4 counts s^{-1} at a 100 ps delay, which is consistent with the expected rate calculated in the preceding paragraph. Since the beam time of the undulator beamline is limited, we could not yet obtain reliable data in the delay range 500–900 ps, throughout which the pump-probe signal must persist. Moreover, the small signal-to-background ratio inhibits us from proceeding to further analysis for fitting the observed data to the theoretical exponential decay of He*($1s2p$ ^1P) convoluted with the temporal profile of the synchrotron radiation pulse. We are now planning to improve the synchrotron radiation photon flux by replacing the Sb of the optical filter by Sn.

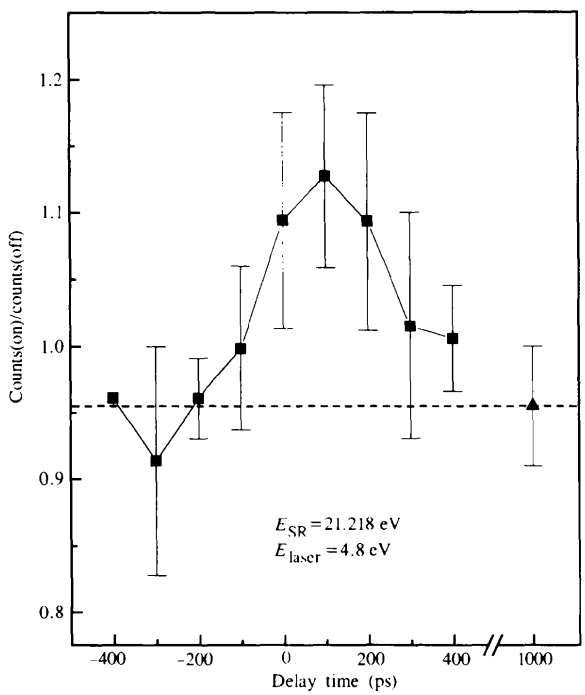

Figure 6
Time-dependent signal of He^+ produced by two-photon ionization of He. The ratio between the ion counts with and without the laser is plotted as a function of the delay of the laser pulse with respect to the undulator pulse. The dashed line represents the background level which is determined from the ratio at 1 ns or longer delays. A broad peak centred around 100 ps results from the pump-probe signal counts due to the two-step transition: the synchrotron radiation excitation from He($1s^2$ ^1S) to He*($1s2p$ ^1P) followed by the laser photoionization. The spectral resolution of synchrotron radiation is set to ~15 meV.

Recently, Larsson *et al.* (1995) have measured the radiative lifetime of He*($1s2p$ ^1P) in a similar two-colour ionization experiment using the 13th harmonic of a tunable Ti:sapphire laser for the first excitation step. The bandwidth of the 13th harmonic light was 4 meV and the overall temporal resolution was limited by the pulse duration, ~50 ps, of a probe laser (the third harmonic of an Nd:YAG laser). The deduced lifetime of He*($1s2p$ ^1P) was 0.57 ± 0.03 ns, which can be converted into a $1s \rightarrow 2p$ oscillator strength of 0.269. The number of efficient photons within the Doppler width was smaller in their 13th harmonic light (~3×10^6 photons s^{-1}) than in the undulator radiation in the present study (~2×10^7 photons s^{-1}). However, Larsson *et al.* (1995) could obtain the lifetime with a much better accuracy by taking advantage of a high temporal resolution of high-order harmonics generated from a picosecond laser.

4. Summary and future prospects

We have developed a novel laser–synchrotron radiation combination system in which a mode-locked Ti:sapphire laser is precisely synchronized with synchrotron radiation emitted from the UVSOR storage ring. The features of our laser system are summarized as follows:

(i) Synchronization is realized with excellent stability at 90.115 MHz, which matches with the frequency of the storage ring in its multi-bunch operation.

(ii) The short temporal width of the laser pulse (<2 ps) provides potentialities that we can follow up on ultrafast phenomena in excited molecules by time-resolved two-photon excitation experiments. Let us suppose that we are observing the radiative lifetime, T_{ion}, of ions produced by synchrotron radiation photoionization of laser-excited neutral molecules using a streak camera. If the decay lifetime of the laser-excited state is as short as the laser pulse width, the overall temporal resolution in measuring T_{ion} is determined not by the duration of the synchrotron radiation pulse but by that of the laser pulse. This method can, however, be applicable to electronic transitions with a large oscillator strength, because of an extremely low ratio of efficient (useful) to total photon flux of synchrotron radiation.

(iii) The laser wavelength can be changed between 243 and 280 nm, when the third harmonic of the Ti:sapphire laser is generated. This allows us to make a wide selection of target molecules and their vibronic states.

We are planning to apply this technique to new spectroscopy of polyatomic molecules. One of the most

important primary goals is to investigate the photodissociation and photoionization dynamics of molecules in a given vibronically excited state. Excitation of an outer-valence electron of halogenated molecules or a π electron of aromatic molecules may be most suitable for the above wavelength range of the laser.

We would like to gratefully acknowledge useful suggestions and continuous support from Mr Eiken Nakamura, Dr Shuji Asaka, Professor Masao Kamada and Professor Hiroyuki Hama of the Institute for Molecular Science (IMS). Our thanks are also due to the members of the UVSOR facility for their valuable help during the course of the experiments. One of the authors (MT) would like to thank Professor Teiichiro Ogawa and Dr Kenji Furuya of Kyushu University for providing an opportunity for him to collaborate on this research project. This work was financially supported by national funds appropriated for special research projects of the IMS and by the Joint Research Program (1995–1996) of the IMS.

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