The generation of a tunable laser emission in the vacuum ultraviolet and its application to supersonic jet/multiphoton ionization mass spectrometry

Tomohiro Uchimura, Takayuki Onoda, Cheng-Huang Lin, and Totaro Imasaka[a]
Department of Chemical Science and Technology, Faculty of Engineering, Kyushu University, Hakozaki, Fukuoka 812-8581, Japan

An optical parametric oscillator and a Ti:sapphire laser are used as a pump source for the generation of high-order vibrational stimulated Raman emission in the vacuum ultraviolet region. This tunable laser is employed as an excitation/ionization source in a supersonic jet/multiphoton ionization/ time-of-flight mass spectrometric study of benzene. The merits and potential advantages of this approach are discussed in this study. © *1999 American Institute of Physics.* [S0034-6748(99)03108-1]

I. INTRODUCTION

Supersonic jet (SSJ) spectrometry provides well resolved structural features, which are useful in the differentiation of closely related analyte molecules with similar electronic spectra.[1–8] A combination with multiphoton ionization/time-of-flight mass spectrometry (SSJ/MPI/TOF–MS) provides additional information, concerning molecular weight, which is of further use in the identification of molecular structure. For optimum use, a narrow-band tunable laser is essential, and a dye laser or other tunable laser such as an optical parametric oscillator (OPO) combined with a frequency doubling system are then typically employed in most studies. However, this approach is not without problems. For example, various organic molecules such as alkanes, carbonyl-containing compounds, or alcohols have absorption bands in the vacuum ultraviolet (VUV) region. Therefore, a tunable VUV laser is required for spectrometric measurements. Although an investigation of jet spectroscopy using a single photon ionization scheme at 125 nm has been reported,[9] the SSJ/MPI/TOF–MS technique has, to our knowledge, not yet been demonstrated (at least successfully) in the VUV region. This is due to the fact that the shortest wavelength, which can be generated by the frequency doubling technique, is limited to ~190 nm.[10–12] This limitation arises from requirements of transparency and phase matching for a nonlinear optical crystal (e.g., beta-barium borate, β-BBO). It is possible to generate tunable laser emissions in the VUV region by means of non-Raman four-wave mixing. The pulse energy which is currently generated by this method is, however, insufficient for the multiphoton ionization of organic molecules. It is well known that stimulated Raman scattering (SRS) and succeeding four-wave Raman mixing (FWRM) can be used for the conversion of a laser frequency by a step of 4155 cm^{-1}. Hydrogen, which is currently used as a Raman medium, is transparent and the dispersion is small from the entire infrared/visible to the VUV region, and, as a result, it is possible to generate a tunable laser emission down to the deep-VUV region.[13]

In this work, we investigate the approach of using SRS and FWRM for the efficient generation of a tunable VUV laser, and the application of this VUV source to excitation/ ionization in MPI/TOF–MS.

II. EXPERIMENTAL APPARATUS

A. Lasers and wavelength conversion system

Figure 1 shows the experimental apparatus for the generation and measurement of stimulated Raman emission using the second harmonic emission of an optical parametric oscillator (Spectra-Physics, MOPO-730, 250 nm, 10 mJ, 6 ns, 0.2 cm^{-1}). The UV pump beam is focused onto a Raman cell, which consists of a stainless steel tube and two flanges with windows on both sides. When the conditions of beam focusing are changed, the stainless steel tube is replaced with tubes having different lengths, in order to avoid optical damage of the window material. The emission spectrum of the generated beam is measured by a VUV monochromator (ARC, VM-502, 30–600 nm, maximum at 120 nm) equipped with a VUV photomultiplier (Hamamatsu, R1459, 115–200 nm, maximum at 140 nm), and the resulting signal is processed by a boxcar integrator, which is combined with a recorder or a personal computer through a general purpose interface bus interface.

The third-harmonic emission of a Nd: yttrium– aluminum–garnet (YAG) laser (Spectra Physics, GCR-200, 355 nm, 400 mJ, 6 ns, single longitudinal mode, 0.06 cm^{-1}) was also used for the generation of higher-order anti-Stokes Raman emission. The pulse energy was adjusted to 100 mJ, to avoid optical damage to the window material. A picosecond Ti:sapphire laser (Spectra-Physics, Tsunami, 800 nm, 50 mJ, 100 ps, 50 mJ) was also utilized as a tunable pump source. The second-harmonic emission (400 nm) generated by passing the beam through a potassium dihydrogenphosphate (KH_2PO_4, KDP) crystal was employed for the generation of high-order anti-Stokes Raman emission.

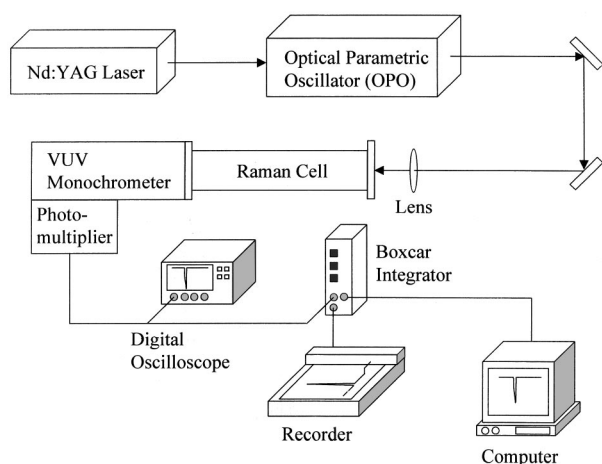[a]Electronic mail: imasaka@apan.cstm.kyushu-u.ac.jp

FIG. 1. Experimental setup for the generation and the detection of high-order anti-Stokes emission.

B. Mass spectrometer

The experimental setup for SSJ/MPI/TOF–MS, in which a VUV laser source is utilized, is shown in Fig. 2. The Raman cell is interfaced with a vacuum chamber, which contains a CaF_2 Pellin Broca prism at the center, in order to separate the multiline Raman emission. The laser beam is focused with a CaF_2 lens, which is placed in front of the prism, into the sample molecule in the jet. This vacuum chamber is further connected to a vacuum system for SSJ spectrometry via a stainless steel tube. The details of the SSJ spectrometer used in this study has been reported previously.[6–8]

C. Measurements

The third-order anti-Stokes emission (AS3, 190.6 nm) generated using the second-harmonic emission (250 nm) of the OPO laser is used for multiphonon ionization (MPI) of benzene which is introduced into the vacuum system from a pulsed nozzle to form a SSJ. Ions induced by VUV radiation are then accelerated by a repeller and grids into a TOF tube and are subsequently detected using an assembly of three microchannel plates (Hamamatsu, F1094-31S). The mass
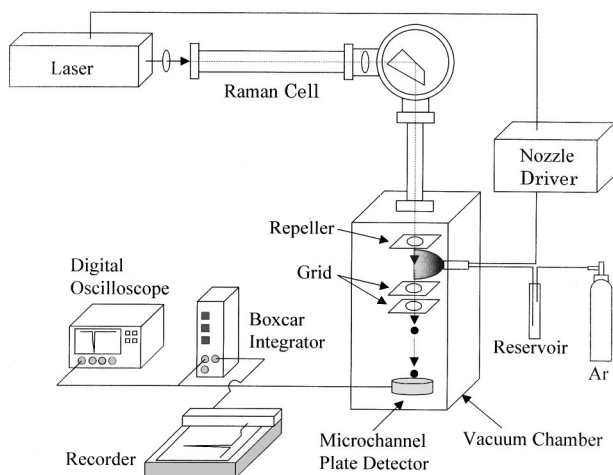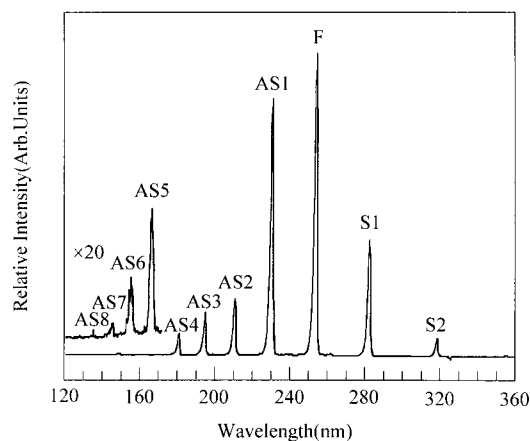

FIG. 2. Experimental setup for SSJ/MPI/TOF–MS.

FIG. 3. Spectrum for multiline stimulated Raman emission generated via an OPO laser.

spectrum is recorded by a digital oscilloscope (LeCroy 9360, 600 MHz). The MPI spectrum is measured by a boxcar integrator, interfaced with a recorder.

III. RESULTS AND DISCUSSION

A. OPO laser

The spectrum of the multiline Raman emission obtained using the second-harmonic emission of the OPO laser is shown in Fig. 3. Optimum values for the focal length of the lens and the hydrogen pressure were 500 mm and 10 atm, respectively. Under these conditions, it is possible to extend the wavelength of the laser to 136.5 nm (8th anti-Stokes emission, AS8). The OPO laser is tunable in the range of 440–670 nm for a signal beam (from 750 nm to 2000 nm for an idler beam), and the wavelength is extended from 220 to 335 nm by frequency doubling. The tunable range, which can, in practice, be used for the generation of the stimulated Raman emission, is, however, in the range from 230 to 320 nm. Thus, the laser wavelength can be scanned from 130.3 nm (AS8) to 435.9 nm (S2) with no gaps. However, the pulse energy decreases rapidly below AS5 (164.5 nm). Therefore, the practical limit of the shortest wavelength which can be applied to SSJ spectrometry may be ~176.6 nm (AS4) under the conditions described herein.

B. Nd:YAG laser

In order to demonstrate the potential advantages of this approach, we tentatively used a Nd:YAG laser (355 nm) as a pump beam for the efficient generation of high-order anti-Stokes emission below 170 nm. In Fig. 4, the relative intensity of the high-order anti-Stokes Raman emission generated is plotted down to 13th-order (121.6 nm). Although the pulse energies are not calibrated, the intensity distribution is rather flat. Such a favorable result might be obtained as the result of a high pulse energy (100 mJ), a narrow linewidth (0.06 cm^{-1}), and a good beam quality ($M^2 = 1.66$) of the Nd:YAG laser used, since it is injection seeded with a high-beam-quality diode-laser-pumped Nd:YAG laser. The optimum
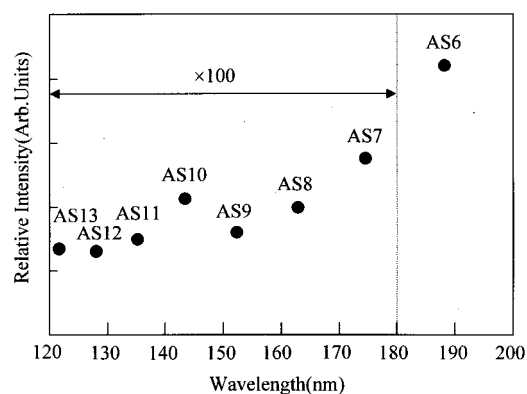
FIG. 4. Pulse energy of high-order anti-Stokes emission generated via a Nd:YAG laser.
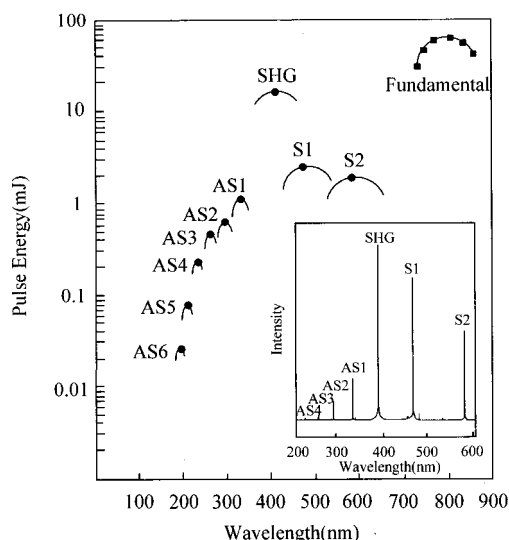

FIG. 5. Pulse energy of high-order Stokes and anti-Stokes emission generated via a second-harmonic generation Ti:sapphire laser. The tuning range of the fundamental Ti:sapphire laser is also indicated in the figure. The emission spectrum is inserted in the figure.

values for the focal length of the lens and the pressure of hydrogen were determined to be 1 m and 1.5 atm, respectively. The shift in optimum conditions can be explained by (1) a high pulse energy and (2) a narrow linewidth of the laser; since (1) a long confocal distance and a large beam waist size are required to avoid breakdown of the hydrogen gas and (2) a Raman linewidth narrower than the laser linewidth, which can be achieved by reducing the hydrogen gas pressure, is desirable, in order to enhance the Raman gain. It is reasonable to assume that the present VUV source would be applicable down to 120 nm. Although a Nd:YAG laser is not tunable, the laser frequency can be changed by a step of 4155 cm^{-1}, which corresponds to ~15 nm in the VUV region. Thus, it appears to have the potential for use in spectrometric measurements when step tunability is acceptable. A strong VUV beam of AS6 (188.2 nm) could be observed in air, although it rapidly became weak with continued propagation. Thus, a vacuum system is needed for wavelengths below ~200 nm, in order to remove oxygen from the air. The energy of the third-harmonic emission of the Nd:YAG laser can be increased to 400 mJ, at which conditions it might be possible to increase the pulse energy of the high-order anti-Stokes Raman emission, although the length of the Raman cell (and the optical table as well) needs to be increased further to avoid optical damage of the window material.

C. Ti:sapphire laser

In order to improve the efficiency for the generation of high-order anti-Stokes Raman emission, a laser capable of generating a high peak power is preferred, since SRS and FWRM are nonlinear optical effects. A Ti:sapphire laser is tunable in the range from 750 to 950 nm and the pulsewidth can be reduced to picoseconds by mode locking. Figure 5 shows the tunable range of the Raman emission obtained by using a fundamental beam (800 nm) and that obtained by the second-harmonic emission (400 nm). The pulse energies were measured down to AS6, while AS7 and AS8, whose pulse energies are estimated to be the order of microjoules, could be visually confirmed. In practical terms, the tunable range of the present Ti:sapphire laser is limited to 760–840 nm due to the effective bandwidth of the dielectric coatings

used for mirrors, *Q* switches, and lenses. It is well known that conversion efficiencies are strongly enhanced at shorter wavelengths in SRS and FWRM. Thus, the third-harmonic emission of the Ti:sapphire laser may be desirable for more efficient generation and for wider spectral coverage in the VUV region, although a more complicated autotracking system would be required for wavelength tuning. The present approach using a short laser pulse, with respect to SSJ spectrometry is attractive. For example, it has been reported that ionization efficiency is greatly improved by reducing the laser pulsewidth, for cases of samples with short lifetimes, e.g., polychlorinated dioxins and their precursors.[7] Thus, a laser with a narrow linewidth and a short pulsewidth, i.e., a picosecond Fourier transform-limited pulse (e.g., 0.01 nm, 10 ps), is preferred for selective, as well as efficient ionization in SSJ spectrometry. Because of this, a VUV laser obtained using a mode-locked Ti:sapphire laser may be advantageous in the spectroscopic analysis of such compounds.

D. Application to MPI/MS

In order to demonstrate the validity of the VUV laser developed in this study, the present VUV laser was tested as an excitation/ionization source in SSJ/MPI/TOF–MS. Figure 6 shows the excitation and resulting ionization/dissociation pathway for benzene. It is known that this relaxation pathway depends on the total energy, i.e., the total number of photons which are absorbed by a molecule. In such studies, a tunable VUV laser is required, for the investigation of the dynamic processes. A mass spectrum, in which the laser wavelength is adjusted to 190.6 nm (6.51 eV, 1.9 μJ), is shown in Fig. 7. The dominant ions in this spectrum are fragment ions. The mass spectrum obtained by propagating the beam in air is also shown in Fig. 8. In this case, the pulse energy was too small to be measured by a joulemeter, since the beam was attenuated by room air. In this spectrum, the fragment ion peaks are relatively smaller than the molecular
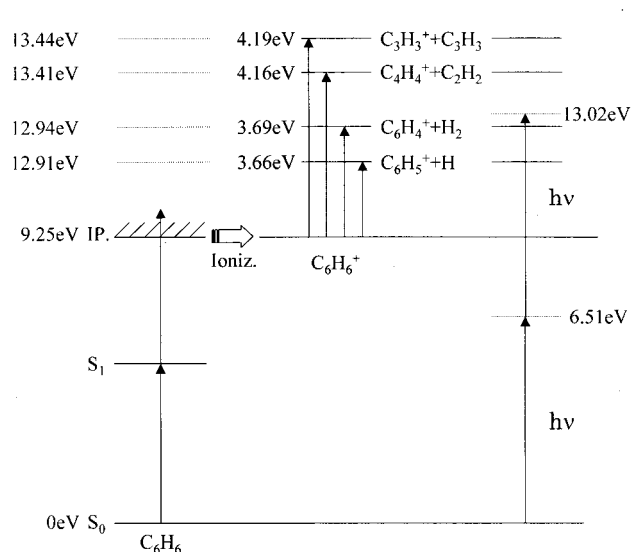
FIG. 6. Excitation/ionization/dissociation pathway of benzene.

FIG. 8. Mass spectrum for benzene measured by SSJ/MPI/TOF–MS. The experimental conditions are same as those in Fig. 7, but the laser beam is transmitted (and attenuated) in air.

ion peak. This is probably due to the low pulse energy for the transmitted beam in air, since the fragment ions are more abundant at high pulse energies. The technique based on SRS–FWRM and open-air beam propagation has already been employed in SSJ spectrometry for spectrometric measurements in the range of 202.5–198.5 nm.[14] Needless to say, a vacuum-tight system is desirable for retaining sufficient pulse energies of the VUV beam below 195 nm. In any case, fragment ions are clearly observed in the mass spectrum. This indicates that the total energy derived by the absorption of VUV photons is sufficient for the ionization and dissociation of benzene. It has been reported that the ionization energy for benzene is 9.25 eV.[4] In order to observe fragments such as $C_4H_4^+$ and $C_3H_3^+$, the wavelength of the VUV beam should be shorter than 184.9 and 184.5 nm, respectively, providing a molecule absorbs only two photons in the process of producing these ions. In this experiment, these fragment ions are observed even by using VUV photons of 190.6 nm. 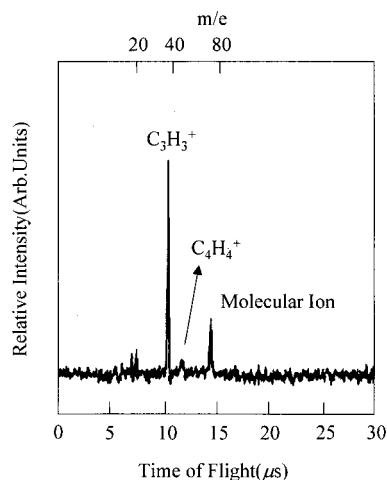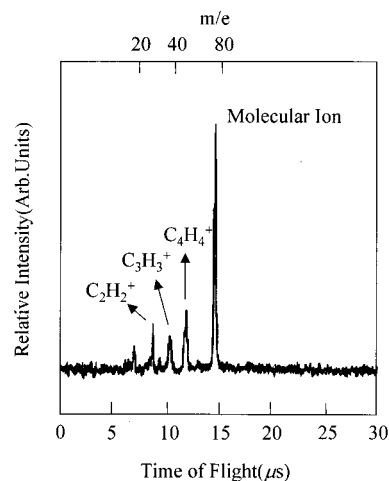Thus, it is likely that more than three photons are absorbed for the reactions shown in Fig. 6. It has been reported that the threshold for the dissociation of benzene is nearly identical to the total energy of two photons (13.0 eV).[15] Thus, it may be necessary to take into account the dissociation and succeeding fragment ionization process as well. Although more detailed and careful investigation is necessary in this area, the present tunable VUV laser may provide valuable information for spectroscopic studies which involve ionization and dissociation pathways.

Ketones and aldehydes have absorption bands ($\pi \rightarrow \pi^*$) in the VUV region, i.e., ~188 and 180 nm, respectively. Similarly, aliphatic hydrocarbons have absorption bands ($\sigma \rightarrow \sigma^*$) at higher energies, e.g., ~135 nm for propane. For spectrometric studies of such compounds, it would be necessary to more efficiently generate higher-order anti-Stokes emission. It has already been reported that high-order anti-Stokes emission are enhanced by nearly two orders of magnitude in the far VUV region by using Stokes emission as a seed beam and by using a hydrogen gas cooled to a liquid-nitrogen temperature as a Raman medium.[16–18] More simply, it is possible to enhance the efficiency by multiple passes of the fundamental and Raman beams in a Raman cell.[19,20] Such approaches may permit the recording of a MPI/MS spectrum for various compounds in the VUV region.

It is sometimes necessary to use two different photons in excitation and succeeding ionization, since the ionization potential is, in some cases, much larger than twice of the energy used for excitation, especially for cases of large polycyclic aromatic hydrocarbons.[6] In this case, two independent lasers are currently used for two-color MPI. In such a case, however, aligning the beams is not an easy task, since they need to be exactly matched, both temporally and spatially. A beam which contains strong fundamental (or low-order anti-Stokes) and weak anti-Stokes (or higher-order anti-Stokes) emissions may be employed as a two-color beam for excitation and the succeeding ionization, respectively. It should be noted that the ionization laser should be sufficiently weak to avoid single-color ionization via congested high vibrational

FIG. 7. Mass spectrum for benzene measured by SSJ/MPI/TOF–MS. The AS3 emission (190.6 nm, 1.9 μJ) generated by using the OPO laser (250 nm, 8.9 mJ) is used for MPI.

levels of the excited state. When this requirement is met, the earlier combination is suitable for two-color MPI, in contrast to the case where a more complicated (and expensive) two-color laser system is used. Thus, SRS and FWRM techniques appear to be potentially useful in overcoming some of the current problems in SSJ spectrometry.

ACKNOWLEDGMENT

[1] V. H. Grassian, E. R. Bernstein, H. V. Secor, and J. I. Seeman, J. Phys. Chem. **94**, 6691 (1990).

[2] C. Weickhardt, R. Zimmermann, U. Boesl, and E. W. Schlag, Rapid Commun. Mass Spectrom. **7**, 183 (1993).

[3] J. W. Hager and S. C. Wallace, Anal. Chem. **60**, 5 (1988).

[4] R. Tembreull, C. H. Sin, P. Li, H. M. Pang, and D. M. Lubman, Anal. Chem. **57**, 1186 (1985).

[5] B. Kim and P. M. Weber, J. Phys. Chem. **99**, 2583 (1995).

[6] C. H. Lin, M. Hozumi, T. Imasaka, and N. Ishibashi, Analyst (Cambridge, U.K.) **116**, 1037 (1991).

[7] J. Matsumoto, C. H. Lin, and T. Imasaka, Anal. Chem. **69**, 4524 (1997).

[8] T. Imasaka, M. Hozumi, and N. Ishibashi, Anal. Chem. **64**, 2206 (1992).

[9] M. S. de Vries and H. E. Hunziker, J. Photochem. Photobiol., A **106**, 31 (1997).

[10] W. L. Glab and J. P. Hessler, Appl. Opt. **26**, 3181 (1987).

[11] W. Mückenheim, P. Lokai, B. Burghardt, and D. Basting, Appl. Phys. B: Photophys. Laser Chem. **45**, 259 (1988).

[12] B. Wu, F. Xie, C. Chen, D. Deng, and Z. Xu, Opt. Commun. **88**, 4571 (1992).

[13] H. Morikawa, S. Wada, H. Tashiro, K. Toyoda, A. Kasai, and A. Nakamura, J. Appl. Phys. **74**, 2175 (1993).

[14] J. A. Ayage, Anal. Chem. **62**, 505 (1990).

[15] H. Kühlewind, A. Kiermeier, and H. J. Neusser, J. Chem. Phys. **85**, 4427 (1986).

[16] A. Goehlich, U. Czarnetzki, and H. F. Döbele, Appl. Opt. **37**, 8453 (1998).

[17] H. Wallmeier and H. Zacharias, Appl. Phys. B. Photophys. Laser Chem. **45**, 263 (1988).

[18] H. Moriwaki, A. Nakamura, S. Wada, and H. Tashiro, Appl. Phys. B: Lasers Opt. **61**, 319 (1995).

[19] S. Ohtake, S. Yoshikawa, and T. Imasaka, Appl. Opt. **34**, 4337 (1995).

[20] T. Imasaka, S. Yamanishi, S. Kawasaki, and N. Ishibashi, Appl. Opt. **32**, 6633 (1993).