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Tunable Vacuum-Ultraviolet Radiation Generated by Two-Photon Resonant Difference-Frequency Mixing in Kripton

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Abstract

Two-photon resonant third-order difference-frequency conversion ($\bar{\omega}_{\mathrm{VUV}} = 2\ \bar{\omega}_{\mathrm{R}} - \bar{\omega}_{\mathrm{T}}$) of powerful two pulsed lasers was studied in the rare gas, Kr. The frequency $\bar{\omega}_{\mathrm{R}}$ provided by a frequency-doubled pulsed dye laser was resonant with the Kr two-photon transitions $4p$ – $5p$[5/2, 2], $4p$ – $5p$[3/2, 2], or $4p$ – $5p$[1/2, 0]. For tunable OPO(optical parametric oscillation) laser radiation $\bar{\omega}_{\mathrm{T}}$ at λ_{T} = 258 – 690 nm, $\bar{\omega}_{\mathrm{VUV}}$ was broadly tunable in the spectral range of λ_{VUV} = 126 – 180 nm when the two-photon transition $4p$ – $5p$[1/2, 0] (λ_{R} = 212.55 nm) was applied. As an application, the VUV(vacuum ultraviolet) wavelength dependence of $C_6H_6^+$ production at around the ionization region (135 – 132 nm) of C_6H_6 was preliminarily measured using the developed TOF(time-of-flight)-MASS spectrometer including a built-up tunable VUV pulse laser as ionization source.

Key Words: *two-photon resonant third-order difference-frequency conversion, vacuum ultraviolet, pulsed dye laser, OPO laser, single-photon ionization, kripton*

1. Introduction

Photochemistry and photophysics in the wavelength region of vacuum ultraviolet (VUV, 100 – 200 nm) have been extensively studied because of their basic information directly relating to valence electrons and chemical bonds.[1, 2] Although a synchrotron orbital radiation (SOR) has become recently available as an intense tunable VUV light source, instead of the conventional VUV light source such as rare gas discharge lamp, its scale is too large for researchers of chemistry or spectroscopy to use it easily at a laboratory level. The results of a large number of investigations since 1967 show that frequency mixing of powerful laser light generates intense VUV and XUV(extreme ultraviolet) radiation with tunable frequency and high spectral brightness.[3 - 5] The development of frequency mixing techniques has made the use of tunable VUV light relatively easy in the research field of photochemistry and photophysics, as a light source of photolysis, spectroscopy, or photoionization.

Transition metal center has been well known to play an important role in enzymatic and catalytic processes.[6] It is useful for a basic understanding of these processes to investigate the interaction between transition metal center and small molecules. Especially, it is of great interest to verify whether or not the chemical bond of the molecule is activated merely at the metal center. In other words, we wish to confirm whether physical (1) or chemical (2) adsorption occurs in the coordination process, as follows:.

$$\text{M (metal center)} + \text{AB (small molecule)} \rightarrow \text{M(AB)} \tag{1}$$
$$\rightarrow \text{MA} + \text{B (or MB} + \text{A)} \tag{2}$$

An experimental approach to this problem is the direct detection of M(AB) by MASS spectroscopy without any fragmentation. However, the reaction product M(AB) must be ionized in the vicinity of the ionization threshold because the coordination bond between metal (M) and ligand (AB) is expected to be very weak compared with a normal chemical bond. Most of the ionization thresholds of transition metal compounds have been reported to lie in the VUV photon energy region (100 – 200 nm).

In this paper, we will report results of tunable VUV light generation by two-photon resonant third-order difference-frequency conversion ($\bar{\omega}_{VUV} = 2\ \bar{\omega}_R - \bar{\omega}_T$) of powerful two pulsed lasers in Kr, as a part of our continuing investigations of transition metal chemistry in the gas phase.

2. Experimental

Figure 1 shows a schematic of the experimental setup used for broadly tunable VUV generation by two-photon resonant third-order difference-frequency conversion in Kr by using two intense pulsed lasers simultaneously excited by a pulsed Nd:YAG laser (Spectra-Physics GCR-290-10).

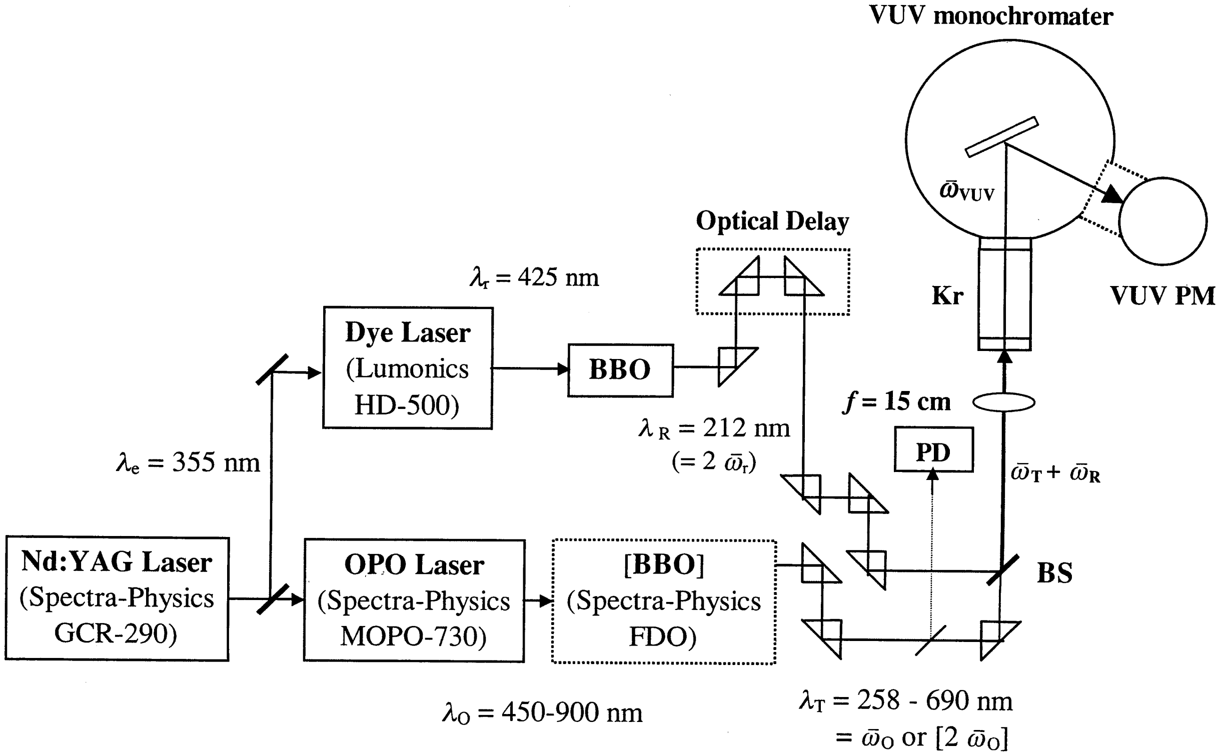

Fig. 1 Schematic of the experimental setup for VUV generation by two-photon resonant third-order difference-frequency mixing in Kr.

The radiation, with frequency $\bar{\omega}_{UV}$ (λ_{UV} = 424.7 – 433.2 nm), is provided by a pulsed dye laser (Lumonics HD-500) operated with Stilbene 420 excited by the pulsed Nd:YAG laser). UV radiation at the two-photon resonant wavelength of Kr is generated by frequency doubling ($\bar{\omega}_R$

$= 2\ \bar{\omega}_{\mathrm{UV}}$) in a β-BaB_2O_4 (BBO) crystal mounted in an autotracker (Lumonics HT-1000). The output power for $\bar{\omega}_R$ is ~100 kW (~1 mJ/pulse). Tunable laser light at the wavelengths λ_T = 258 – 690 nm is provided by an OPO laser system with a frequency doubling option (Spectra-Physics FDO) excited by the same Nd:YAG laser. Typical output powers for $\bar{\omega}_T$ are ~2 MW (~20 mJ/pulse) for the signal light and ~1 MW (~10 mJ pulse^{-1}) for the idler light. The doubling efficiency of the FDO is ~5 – 10 %. For the difference-frequency mixing, the laser beams of both systems (λ_R and λ_T) are spatially superimposed by a suitable dichroic beamsplitter (BS; Sigma Koki Co.), which transmits the wavelength longer and reflects the wavelength shorter than ~260 nm, and focused by a convex lens (f = 15 cm) into a stainless-steel cell (20-cm length) that contains Kr gas. The gas pressure is monitored by an absolute pressure gage (MKS Baratron type 122-1000). The gas cell (with entrance window of fused Quartz and exit window of LiF) is mounted onto the entrance slit of a 0.2-m VUV monochromator (Acton Research Co., VM-502). A solarblind photomultiplier (VUV PM; Hamamatsu R972) attached to a TOF Mass chamber is used for the detection of the generated VUV light. The output of the photomultiplier is recorded with a digital oscilloscope (Tektronix TDS320) and the digitized output is stored and analyzed by a personal computer.

In this study, VUV radiation is generated by two-photon resonant third-order frequency mixing in Kr gas. In Fig. 2, basic diagram for the process is given illustrating energy conversion. In two-photon resonant four-wave mixing process, the nonlinear medium (Kr in this study) is simultaneously irradiated by two laser beams. The beams are composed of the two-photon resonant beam (at frequency $\bar{\omega}_R$) and the tunable different beam (at frequency $\bar{\omega}_T$). Two-photons of frequency $\bar{\omega}_R$ are mixed with a photon of frequency $\bar{\omega}_T$, through the third-order susceptibility $\chi^{(3)}$, to generate a stimulated photon of frequency $\bar{\omega}_{\mathrm{VUV}}$.

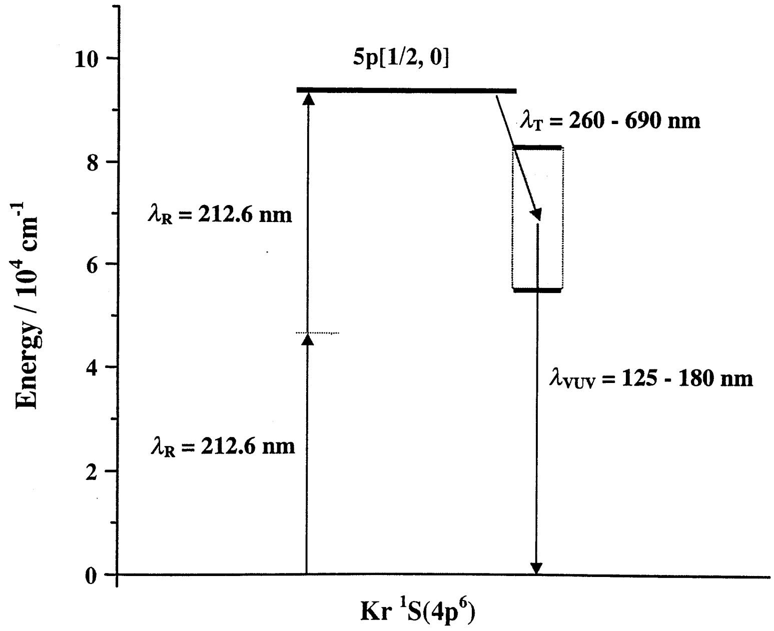

Fig. 2 Energy level diagram related to two-photon resonant third-order difference-frequency mixing in Kr.

$$\bar{\omega}_{\mathrm{VUV}} = 2\ \bar{\omega}_R - \bar{\omega}_T \quad (3)$$

Tunable wavelength regions of OPO laser are 450 – 690 nm (signal) and 730 – 1800 nm (idler), and their doubling of 225 – 345 nm and of 365 – 900 nm, respectively. Applying Kr[1/2, 0] level to the two-photon resonance, the difference mixing will give $\bar{\omega}_{\mathrm{VUV}}$ of 201 – 120 nm.

Relative conversion efficiencies of the third harmonics $\bar{\omega}_{\mathrm{VUV}} = 3\ \bar{\omega}_{\mathrm{R}}$ generated with UV laser radiation at $\bar{\omega}_{\mathrm{R}}$ in Kr are summarized in Table 1 in comparison with Xe data,[7, 8)] suggesting that the frequency mixing, involving the 5*p*[1/2, 0] level of Kr, is more advantageous because of its high efficiency. As easily noticed from Table 1, the wavelength required for two-photon resonant to 5*p*[1/2, 0] level is the shortest (λ_{R} = 212.5 nm), which has not been obtainable by the use of conventional nonlinear optical materials such as KDP or KB5, so far. Considerably higher efficiencies ($\lesssim$ 15 %) are now obtainable with the new nonlinear optical material BBO. Besides producing high conversion efficiency, this material generates the second harmonic of radiation at a wavelength as short as 410 nm. In this study, the transition 4*p* – 5*p* [1/2, 0] (λ_{UV} = 212.5 nm) was mainly used for two-photon resonant mixing, in addition to the 4*p* – 5*p* [5/2, 2] transition (λ_{UV} = 216.7 nm) or the 4*p* – 5*p* [3/2, 2] transition (λ_{UV} = 214.8 nm), because the use of this transition is particularly advantageous owing to its considerably high conversion efficiency.

Table 1 Relative efficiency of two photon resonant third-order frequency mixing in a rare gas (Kr and Xe) as nonlinear media

Nonlinear media	Two photon resonant level	Level energy / cm^{-1}	Resonance wavelength / nm (cm^{-1})	Relative efficiency
^{36}Kr	5p [5/2, 2]	92308.177	216.666 (46154.089)	167
(4p)	5p [3/2, 2]	93124.140	214.767 (46562.070)	56
	5p [1/2, 0]	94093.662	212.554 (47046.831)	1000
^{54}Xe	6p [5/2, 2]	78120.303	256.015 (39060.152)	~ 300
(5p)	6p'[3/2, 2]	89162.880	224.309 (44581.440)	40
	7p [3/2, 2]	88352.201	226.367 (44176.101)	9
	7p [1/2, 0]	88842.781	225.117 (44421.391)	26

3. Results and Discussion

When a two-photon resonant beam (λ_{R} = 212.4554 nm) and a tunable different beam (λ_{T} = 690.0 nm) were simultaneously focused by a convex lens (f = 15 cm) into a 200-Torr Kr cell, a 129.154-nm radiation was generated through the two-photon resonant third-order frequency conversion. Its time-profile is shown in Fig. 3, which is very similar to the Nd:YAG laser pulse figure. It was checked by the following experimental procedures whether or not the generated light can be considered as a coherent VUV radiation:

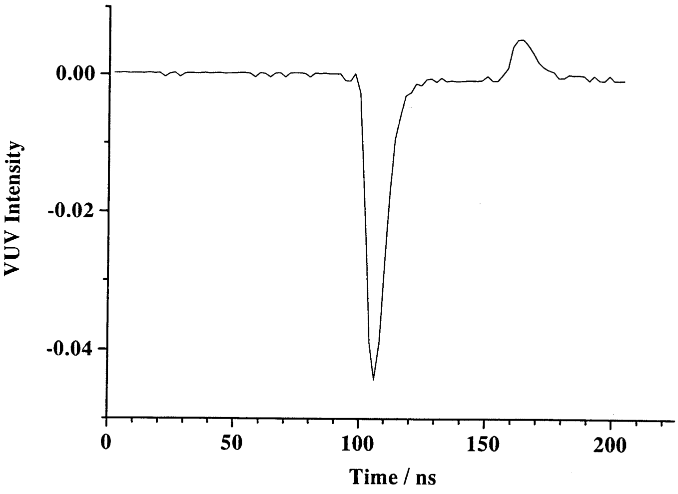

Fig. 3 Typical time profile of VUV light generated by two-photon resonant third-order difference-frequency mixing in Kr using two intense pulsed lasers.

a) No generated light could be observed when the light of $\bar{\omega}_R$ was cut off.
b) No generated light could be observed when the light of $\bar{\omega}_T$ was cut off.
c) No generated light could be observed when the convex lens was removed.
d) No generated light could be observed when the Kr gas was pumped out from the cell.
e) No generated light could be observed when the wavelength of the VUV monochromator was tuned off by ~ 10 nm when the slit width was ~ 1 mm corresponding to the spectral resolution of ~ 4 nm).

From these experimental evidences, it was concluded that the observed light was a coherent VUV radiation generated by a two-photon third-order different-frequency conversion.

Figure 4 shows the measured dependence of the VUV output power P_{VUV} at λ_{VUV} = 134.96 nm on Kr pressure. The solid curve is a theoretical fitting, applicable to this type of mixing, which can be represented by the following equation:[9]

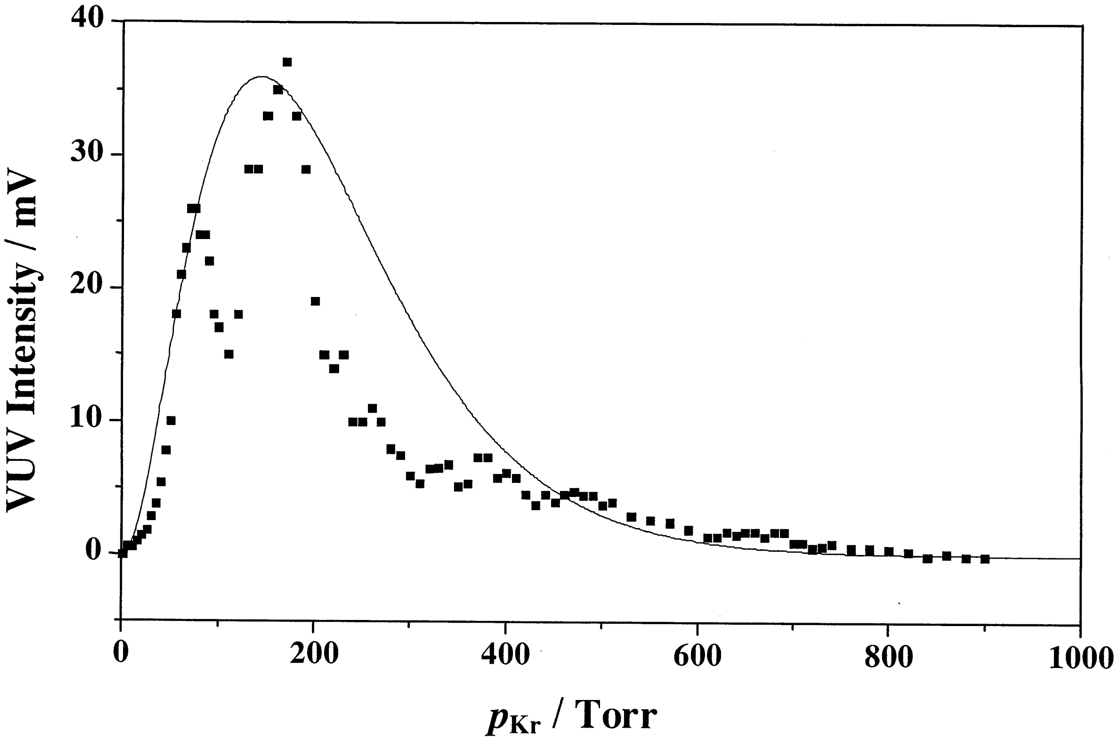

Fig. 4 Generated VUV intensity at λ = 134.96 nm as function of the Kr gas pressure: λ_R = 212.428 nm, λ_T = 500.000 nm, f = 15 cm. The solid line is a theoretical curve (cf. text).

$$P_{VUV}(N) \propto I_R^2 I_T p_{Kr}^2 \exp(-\alpha f^2 p_{Kr}) \qquad (3)$$

where I_R and I_T are the intensities of the two-photon resonant beam ($\bar{\omega}_R$) and of the different beam ($\bar{\omega}_T$), p_{Kr} is a Kr pressure, α is a constant, and f is the focal length of the convex lens. In these experimental conditions, the optimum Kr pressure was about 200 Torr.

The broad spectral region observed by the frequency $\bar{\omega}_{VUV}$ is shown in Fig. 5. With tunable radiation at λ_T = 690 – 258 nm, the difference frequency conversion $\bar{\omega}_{VUV} = 2\,\bar{\omega}_R - \bar{\omega}_T$ generated VUV light at λ_{VUV} = 125 – 180 nm when the two-photon resonance $4p - 5p$ [1/2, 0] (λ_R = 212.554 nm) was applied. The tunable radiation was provided at λ_T = 690 – 450 nm by the signal light $\bar{\omega}_S$ of the OPO laser, at λ_T = 450 – 366 nm by the doubling frequency $\bar{\omega}_T = 2\,\bar{\omega}_I$ of the idler light

$\bar{\omega}_I$ of the OPO laser (λ_I = 900 – 732 nm), and at λ_T = 345 – 258 nm by the doubling frequency $\bar{\omega}_T = 2\ \bar{\omega}_S$ of the signal light $\bar{\omega}_S$ (λ_S = 690 – 516 nm). These results were measured with different pulse powers of the UV radiation P_R ~100 kW (~1 mJ/pulse) and of the tunable laser light P_T ~2 MW (~20 mJ/pulse) at λ_T = 690 – 450 nm, P_T ~ 0.1 MW (~1 mJ/pulse) at λ_T = 450 – 366 nm, and P_T ~ 0.2 MW (~2 mJ/pulse) at λ_T = 345 – 258 nm. The pressure of Kr gas p_{Kr} was kept constant at 200 Torr. It is important to note that the tuning curves of three tunable laser regions in Fig.4 are not displayed on the same scale. These results only demonstrate the tuning of the generated difference-frequency but provide no information on the wavelength dependence of the output power.

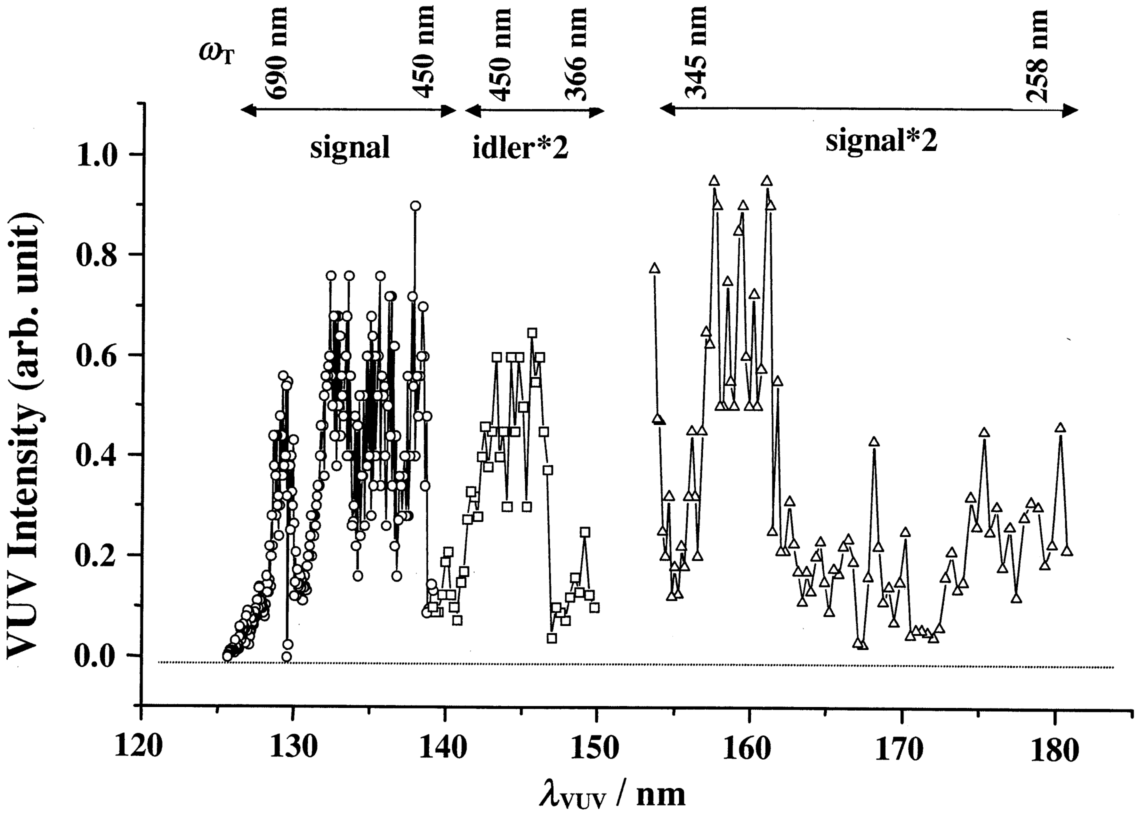

Fig. 5 Wavelength $\bar{\omega}_T$ dependence of the VUV intensity generated at the frequency $\bar{\omega}_{VUV} = 2\bar{\omega}_R - \bar{\omega}_T$ for the following OPO laser output: ○, signal output (450 – 690 nm); △, frequency doubling of idler output (450 – 366 nm); □, frequency doubling of signal output (345 – 258 nm).

The relative power P_{VUV}, detected when λ_R was tuned in the two-photon resonant region of Kr and λ_T was fixed at 500.00 nm, is shown in Fig. 6. In this experiment, the frequency of a Stilbene 420 dye laser was doubled in a suitable BBO crystal. The relative VUV intensity ratio is P_{VUV} (5p[1/2,0]) : P_{VUV} (5p[3/2,2]) : P_{VUV} (5p[5/2,2]) = 1000 : 67 : 133, which is fairly consistent with the theoretical ratio of the output of the resonant third harmonic $\bar{\omega}_{XUV} = 3\ \bar{\omega}_R$ in Kr; P_{XUV} (5p[1/2,0]) : P_{XUV} (5p[3/2,2]) : P_{XUV} (5p[5/2,2]) = 1000 : 11 : 115.[10)] It is clear that the use of the transition 4p – 5p [1/2, 0] is particularly advantageous for the generation of intense tunable VUV light.

Wavelength dependence of $C_6H_6^+$ formation at around the ionization region (135 – 132 nm) of C_6H_6 was preliminarily measured by using a TOF-MASS[11)] spectrometer, including the built-

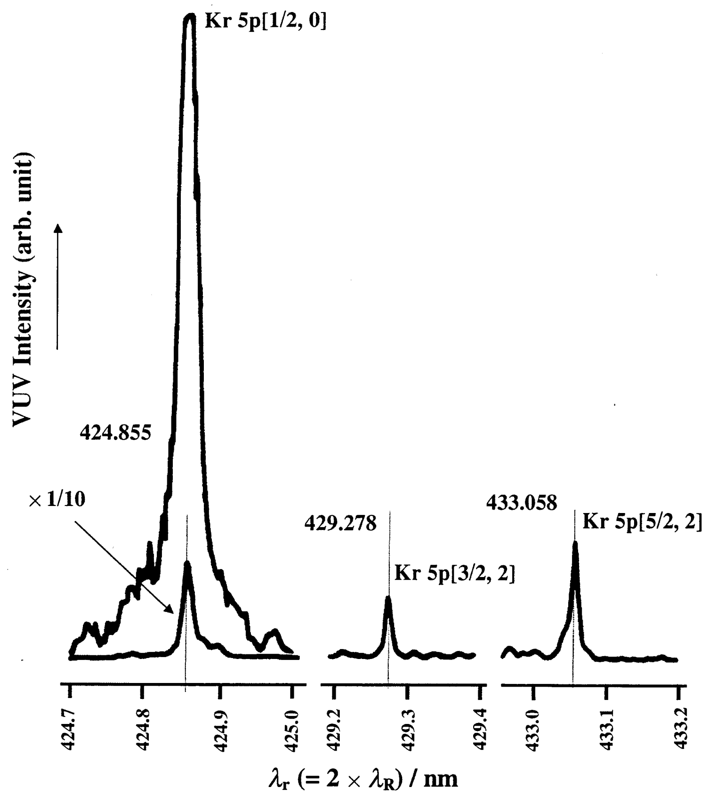

Fig. 6 Wavelength $\bar{\omega}_R$ dependence of the difference frequency $\bar{\omega}_{VUV} = 2\,\bar{\omega}_R - \bar{\omega}_T$ generated in a Kr gas cell. The pressure in the gas cell was 200 Torr.

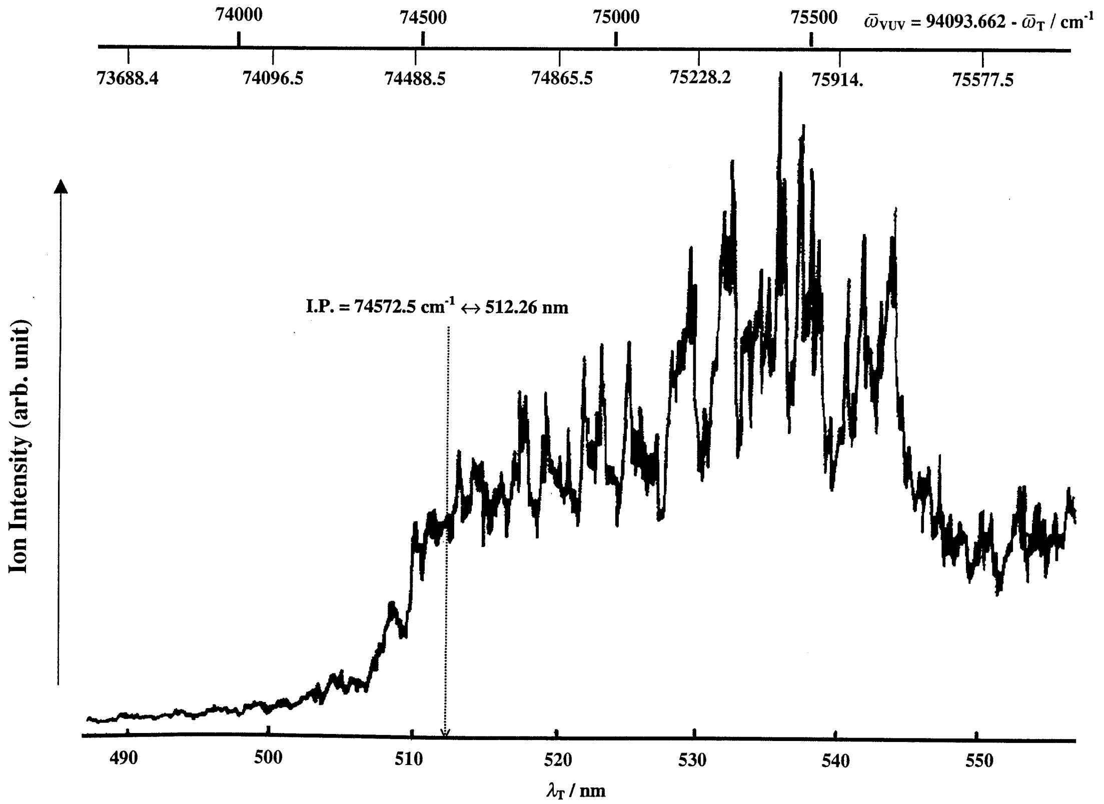

Fig. 7 An application of broadly tunable VUV pulse radiation generated by two-photon resonant third-order frequency conversion in krypton. VUV wavelength dependence of $C_6H_6^+$ ion intensity in the ionization threshold region of C_6H_6 measured by the TOF mass spectrometer.

up tunable VUV pulse laser as an ionization source (Fig. 7). The ionization potential of C_6H_6 is 9.2459 eV (74572.5 cm^{-1}). 12) The one-photon ionization in this threshold region did not produce any ion in addition to the parent ion $C_6H_6^+$, *i.e.* there was no fragment ion, while a typical mass spectrum of C_6H_6 with an electron impact includes some fragment ions.13) The ions produced at photon energy regions lower than the ionization potential might be due to an autoionization of Rydberg states or an ionization of hot molecules.

In this study, a generation of tunable VUV radiation was investigated in order to develop a single photon ionization TOF-MASS with the intention of directly detecting chemical compounds involving relatively weak bonds such as transition metal carbonyls with high sensitivity and without fragmentation. When the frequency $\bar{\omega}_R$ was tuned to the two-photon transition 4p – 5p [1/2, 0], the VUV radiation $\bar{\omega}_{VUV}$ was generated in the wavelength region of 126.7 – 180.7 nm for λ_T = 689 – 258 nm. The spectral width of the VUV light was limited by the linewidth of the OPO-laser radiation ($\Delta\bar{\omega} \sim 0.6$ cm^{-1}). The preliminary TOF-MASS measurement showed that in the single-photon ionization at around the ionization threshold, only a parent ion could be detected with high sensitivity, *i.e.* there was no fragmentation. The built-up TOF-MASS spectrometer with the tunable VUV pulse laser as an one-photon ionization source would be very useful for a highly sensitive direct detection of transient species involving some week bonds, especially of the transition metal coordination compounds.

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References

1) H. Okabe, *Photochemistry of small molecules*, Wiley, New York, 1978.
2) R. Schinke, *Photodissociation Dynamics*, Cambridge University Press, Cambridge, 1993.
3) G. H. C. New and J. F. Ward, *Phys. Rev. Lett.*, 19, 556 (1967).
4) W. Jamroz and B. P. Stoicheff, in "*Progress in Optics*", E. Wolf, ed. North-Holland, Amsterdam, 1983, Vol. 20, pp. 326 – 380.
5) C. R. Vidal, in "*Tunable Lasers*", I. F. Mollenauer and J. C. White, eds. Springer-Verlag, Heidelberg, 1987.
6) J. P. Collman, L. S. Hegedus, J. R. Norton, and R. G. Finke, "*Principles and Applications of Organotransition Metal Chemistry*", University Science Book, California, 1987.
7) R. Hilbig and R. Wallenstein, *IEEE J. Quantum Electron.*, QE-19, 194 (1983).
8) R. Hilbig, A. Lago, and R. Wallenstein, *J. Pot. Soc. Am. B*, 11, 1753 (1987).
9) G. C. Bjorklund, *IEEE J. Quantum Electron.*, QE-11, 287 (1975).
10) D. C. Hanna, M. A. Yuratich, and D. Cotter, "*Nonlinear Optics of Free Atoms and Molecules*", Springer-Verlag, Berlin, 1979.
11) W. C. Wiley and I. H. McLaren, *Rev. Sci. Instr.*, 19, 1150 (1955).
12) K. Kimura, S. Katsumata, Y. Achiba, T. Yamazaki, and S. Iwata, "*Handbook of HeI photoelectron spectra of fundamental organic molecules*", Halsted Press, New York, 1981.
13) NIST Standard Reference Database 69 – 2001: *NIST* Chemistry WebBook.