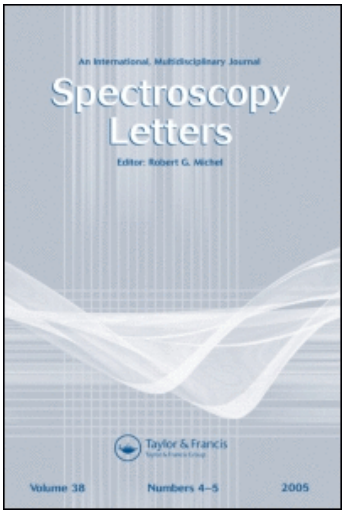

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Nd:YAG Laser-Based Photoacoustic Detection of Ozone: Comparison of Pulsed and Quasicontinuous Wave Operation and Field Tests

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Nd:YAG Laser-Based Photoacoustic Detection of Ozone: Comparison of Pulsed and Quasicontinuous Wave Operation and Field Tests

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Abstract: Sensitivity in the lower ppb range for ozone detection by a photoacoustic system based on a low repetition rate and a quasicontinuous wave (QCW) frequency quadrupled Nd:YAG laser system is demonstrated. The two systems were compared from various points of view such as available UV light power, minimum detectable ozone concentration, photoacoustic signal generation efficiency, as well as simplicity of construction and ease of operation. The QCW-based system was found to have the potential in practical applications due to its relative simplicity and compactness. Therefore, after laboratory calibration it was tested at an environmental monitoring

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station: it was run in parallel with a routinely used ozone measuring instrument, where it showed reliable operation.

Keywords: Photoacoustic spectroscopy, Ozone, Nd:YAG laser, Ultraviolet

INTRODUCTION

Since the pioneering work of Viengerov,[1] who raised the possibility of developing a photoacoustic (PA) gas concentration analyzing instrument, the vast majority of the work dealing with PA gas detection was oriented toward the practical application of the method (i.e., using it for detecting trace components of the earth's atmosphere or of gas mixtures).[2] The selection criteria for light sources in PA systems for practical applications are always threefold: simplicity, wavelength coverage (i.e., how many gas components can be measured quasisimultaneously), and emission bandwidth. The latter becomes fundamental when the analyte is in a complicated gas mixture making selectivity a crucial issue. One family of photoacoustic gas detectors are based on blackbody emitters. These light sources are simple, and their radiation covers a large portion of the mid-infrared wavelength range where most of the molecules have strong absorption bands. Yet, PA systems based on them can hardly meet selectivity requirements. Lasers, on the other hand, are the right choice if selectivity is an important issue. In terms of simplicity and wavelength coverage, however, they are far from being optimal. This explains why selection from the numerous available lasers is always a crucial step when building a photoacoustic system for a given application. Early photoacoustic systems were mainly built on lasers in the UV range,[3] but later almost all efforts on photoacoustic system development were concentrated on infrared gas laser (mainly CO and CO_2) based PA systems.[4] It has been realized, however, that no matter how promising gas laser–based PA systems are, they can hardly get widespread applications—clearly not in field and industrial measurements—due to their complexity in construction and difficulty in operation. Recently, semiconductor diode lasers (SDLs) and quantum cascade lasers (QCLs) received renewed attention in PA system development,[5,6] due to their relative simplicity, long lifetime, and automatic operation. Meanwhile, however, the potential for practical applications of PA systems in general has somewhat declined due to the rapid development of very powerful alternative gas detection instruments, such as gas chromatographs and ion mobility spectrometers. Current PA developments, therefore, focus on areas where the method offers specific advantages over alternative techniques (e.g., by using the above mentioned SDLs and QCLs).

One of the potential application areas for PA systems is the detection of the concentration of ozone, a key substance in the earth's atmosphere.[7] Its presence in the atmosphere is crucially important for the quality of our life. The absorption of solar ultraviolet radiation by stratospheric ozone

(12 to 50 km) protects the biosphere from harmful radiation, while the absorption of the surface-emitted infrared radiation by tropospheric ozone (surface to 12 km) plays an important role in the global temperature balance. The photochemical reactivity of ozone influences the chemical composition of both the stratosphere and troposphere. Altogether, the thermal and chemical characteristics of the lower atmosphere are strongly influenced by the ambient concentration of ozone. Although several satellite- and balloon-borne techniques exist for the measurement of ozone concentration in the higher layers of the atmosphere, monitoring it at the surface of the earth, where it has the most direct and most harmful effect on human health and the environment, is still a burning issue. A variety of measurement techniques has been developed for this purpose.[8] These include UV absorption, DOAS (differential optical absorption spectroscopy), chemiluminescence and chemical titration methods, particularly electrochemical techniques, and LIDAR (light detection and ranging). The UV absorption technique is commonly employed for the routine monitoring of ozone in environmental air primarily because it does not require any reagent gases or liquids (such as in the chemiluminescence method) and, in principle, it is an absolute measurement of ozone concentration. The main disadvantage of the UV absorption technique is that its readings are influenced not only by ambient interferants (most significantly by aromatic hydrocarbons and their oxidation products) but also by calibration uncertainties and by anomalous sensitivity to operating conditions. The caused uncertainties in measured ozone levels are hardly tolerable and must be reduced. The need for frequent recalibration and maintenance of these devices makes the problem even more acute. Recently, ozone detection systems based on mid-infrared QCLs were tested under laboratory conditions.[9,10]

In one of our previous works,[11] it was demonstrated that a photoacoustic system can outperform an optical absorption–based system provided there exists a proper light source usable in the PA system. Such a light source has to be suitable for being modulated at a frequency of a few kilohertz, which is the typical range of the resonance frequency of an acoustically optimized PA cell, or alternatively has to be capable of pulsed operation with a pulse length in the low microsecond range or below. (Theoretically, the resonance frequency of a PA cell can cover a much wider range but in practice, provided that one wants to avoid the use of special and thereby rather expensive microphones or nonpractical resonator geometries, the useful frequency range is limited to the kilohertz region.) Furthermore, the modulated light source must have at least a few milliwatts modulated output power, or alternatively, at least a few tens of microjoules pulse energy. Although a lamp used in an optical absorption based ozone detector is hardly convertible into a high-performance PA system (mainly due to the lack of a proper modulation method), recent developments on Nd:YAG lasers with nonlinear wavelength conversion into the UV range makes them a promising candidate for the targeted application.

In this paper, different schemes for the photoacoustic measurement of ozone concentration by frequency quadrupled Nd:YAG lasers are described. Calibration curves and detection limits (down to low ppb level ozone concentration) are derived. One of the developed systems, having fairly compact construction, was field-tested in continuous measurements of ozone concentration of the ambient air at an environmental monitoring station.

MATERIALS AND METHODS

For better intercomparability, all experiments were based on the same PA system using different excitation schemes and signal processing. The PA cell was a longitudinal acoustic resonator as it is described in Ref. 12. in detail. The PA signal was detected by an electret microphone (Knowles EK-3029, West Sussex, England) attached to the stainless steel tube forming the acoustic resonator within the PA cell. The microphone signal was amplified by a homemade microphone amplifier and was further processed (see below).

Three different types of excitation schemes were constructed, all based on the fourth harmonic (266 nm) of Q-switched Nd:YAG lasers. This absorption wavelength belongs to the Hartley bands of ozone,[13] with maximum absorption cross-section of $1.15 \times 10^{-17}\,cm^2$/molecule at 254 nm (at 22°C) and of $1 \times 10^{-17}\,cm^2$/molecule at 266 nm (at 22°C).

Pulsed System

In the pulsed PA system, the photoacoustic effect is created by a single laser pulse with relatively high energy and processed individually shot-by-shot. From an acoustical point of view, it corresponds to a Dirac-delta excitation of an acoustic resonator. This assumption is quite justified if one compares the 10-ns laser pulse duration with the 4-kHz resonance frequency of the PA cell. The PA signal, therefore, has a temporal shape of a relaxation oscillation (with the oscillation frequency equal to the acoustic resonance of the PA cell, and the rate of the decay corresponding to the quality factor of the acoustic resonance). From an optical point of view, the advantage of the pulsed systems is the high optical intensity that results in high conversion efficiencies into the fourth harmonic.

Light Source

The light source in this system was a flashlamp pumped, Q-switched Nd:YAG laser (Quanta ray, model GSR-190-10, Spectra Physics, Mountain View, CA, USA) optimized for second harmonic generation (532 nm) using intracavity frequency doubling. The laser had 10-Hz pulse repetition rate, and with a pulse duration of about 10-ns FWHM (full width at half-maximum).

Although this laser is rather bulky, its maximum output energy at 532 nm could be as high as 350 mJ. For the PA measurements, the output energy was set to 25 mJ. (It is obvious that the laser, being a part of an ultrashort high-power laser system,[14] is overscaled for our purposes. The aim of these experiments was to test the limits of the pulsed systems. For possible practical realizations, much more compact and cost-effective Nd:YAG lasers are readily available.) The laser light was frequency doubled to 266 nm with a nonlinear Cesium Lithium Borate (CLBO) crystal. Two dichroic mirrors with maximum reflectivity at 266 nm were used to separate the generated UV light from the green one. An aperture was placed in front of the photoacoustic cell to limit the laser beam diameter to about 2 mm, thereby suppressing the scattered light, thus lowering the acoustic background signal generated by wall absorption within the PA cell.

The conversion efficiency for this pulsed system was 12% (from 25 mJ at 532 nm to 3 mJ at 266 nm).

Signal Processing

The amplified microphone signal from the PA cell was fed into a digital oscilloscope (Tektronix TD5 3052B, Beaverton, OR, USA) together with the voltage output of the energy meter (GENTEC ED150, Québec, Canada), which measured the laser energy directly after the PA cell. To improve the signal-to-noise ratio of the measurement and to suppress signal fluctuations due to pulse-to-pulse laser energy variations, the PA signal was averaged and normalized with the laser energy in the following way. Each PA signal was divided by the measured energy of the laser pulse, and typically 100 shots were averaged (i.e., one PA measurement point was produced every 10 seconds). As a basis for comparison of the different measurements, the absolute PA signal is much more appropriate. To obtain the absolute PA signal, we multiplied the normalized signal with the long-term average of the laser energy.

From the averaged and normalized PA signal, a measure of the ozone concentration was deduced, either by taking its peak-to-peak value (i.e., the difference between the maximum positive and negative signals) or by performing FFT (fast Fourier transformation) on it and taking the frequency component having the maximum amplitude (corresponding to the resonance frequency of the PA cell). In both cases, a personal computer was used for recording and storing the results of the calculations.

Modulated Quasicontinuous Wave System

Figure 1 shows the block diagram of the QCW systems. In the modulated QCW system, the pulse repetition frequency of the laser was set to be equal with (acoustic) resonance frequency (3865 Hz) of the PA cell (i.e., one laser

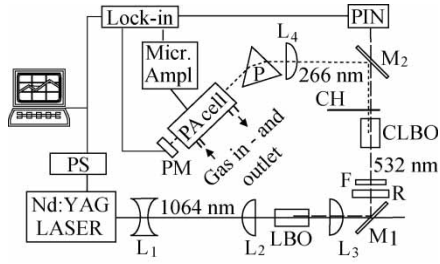

Figure 1. Schematics of the experimental arrangement for the photoacoustic ozone measuring system with a QCW Nd:YAG laser. The following abbreviations are used: PS, power supply for the Nd:YAG laser; L_1, L_2, L_3: lenses with -100-mm, 75-mm, and 50-mm focal length, respectively, for increasing the intensity of the laser beam in the nonlinear crystals; LBO, nonlinear crystal for frequency doubling of the 1064-nm wavelength; M_1, dichroic mirror reflecting at 532 nm; R, $\lambda/2$ plate rotator to set the polarization of the green light for maximum doubling efficiency; F, infrared plate filter; CLBO, nonlinear crystal for frequency doubling of the 532 nm wavelength; CH, chopper for the light modulation (only in case of using the 15-kHz repetition rate); M_2, dichroic mirror reflecting at 266 nm; PIN, pin diode; L_4, lens with 150-mm focal length for focusing the UV light into the resonator of the PA cell; P, fused silica prism; PM, power meter; Micr. Ampl, microphone amplifier. The light paths are indicated by a solid line (for 1064 nm), a dashed line (for 532 nm), and a dotted line (for 266 nm).

pulse per acoustic cycle is used). This corresponds to the resonant excitation of an acoustic mode of the cell.

Light Source

In the modulated QCW system, the light source was a diode-laser pumped, high repetition frequency, Q-switched Nd:YAG laser (Spectra Physics, laser head VHP80-106Q, power supply J20I-8S40-16NSI, Mountain View, CA, USA). The repetition rate of this laser was variable from a few Hz up to 350 kHz. Above this value, the laser was working in continuous mode. Both the maximum output light power and the length of a single laser pulse depended on the pulse repetition rate. At 3865 Hz, the pulse duration was 23 ns. Wavelength conversion was achieved by focusing the near-infrared light to a nonlinear Lithium Triborate (LBO) crystal. The optimum focal spot diameter was achieved by using a combination of two lenses with -100 mm (L_1) and 75 mm (L_2) focal length, respectively. After frequency doubling, the remaining infrared light was eliminated with a dichroic mirror (M_1) with maximum reflectivity at 532 nm and by using an additional infrared filter (F). After rotating the polarization by a $\lambda/2$ plate (R), the green light was focused to a second nonlinear CLBO crystal (the same as the one applied in the previously described pulsed configuration) with a lens (L_3) ($f = 50$ mm). Under these conditions, the Nd:YAG laser delivered 400 mW average power at 1064 nm out of which 1.5 mW was converted into the fourth harmonic.

After the fourth harmonic generation, the remaining green light was filtered out with the combination of a dichroic mirror (M_2) and a 60° fused silica prism (P). After the mirror, a quartz lens (L_4) with 150-mm focal length was used to send the UV light through the PA cell such that the beam diameter of the UV light in the cell was around 2 mm. (The same PA cell was used as previously.) After the PA cell, the laser beam entered a power meter (PM) (Power Max 5200, Molectron, Portland, OR, USA).

Signal Processing

After amplification of the microphone signal with the same microphone amplifier as in the pulsed system, the PA signals were measured with a lock-in amplifier (EG&G Instruments model 5110, Princeton, NJ, USA) and recorded by a personal computer. The time constant (i.e., averaging time) was set to 3 s. At 3865 Hz repetition rate, the reference signal for the lock-in amplifier was provided by the second harmonic of the laser detected with a PIN diode (ET 2010, Electro-Optics Technology, Traverse City, MI, USA).

Chopped Quasicontinuous Wave System

This system was identical with modulated QCW as described in the previous section with the only difference that the laser was run at 15 kHz. The rationale behind this is the following. The laser emits the highest output power at the fundamental wavelength when it is run at the highest repetition rate. As it was mentioned earlier, the pulse duration increases with the repetition rate. From this, it follows that the peak intensity—which is the fundamental parameter in the nonlinear frequency conversion processes—decreases. Consequently, there is an optimum frequency (15 kHz in our system) for the highest fourth harmonic power, which was 5.5 mW. In this case, however, an additional chopper is needed to introduce the necessary modulation at the acoustic frequency (i.e., 3865 Hz). The chopper (model 300CDU, Scitec Instruments, Switzerland) was inserted right after the fourth harmonic generation crystal.

The signal processing was the same as in the modulated QCW system with the only difference that the reference signal for the lock-in amplifier was obtained from the reference output of the chopper controller.

RESULTS

Calibration

For the laboratory calibration of the PA systems, a portable ozone generator (model 175, Thermo Environment Instruments Inc., Franklin, MA, USA)

was used. This calibrator was previously checked and calibrated by the accredited Reference Laboratory of the Hungarian Environmental Institute. The feed gas of the generator was synthetic air from a cylinder with certified purity of 99,999%. Ozone concentration from 0 to 170 ppb was prepared in a randomly selected sequence. Throughout the measurements, a gas flow rate of 200 cm^3/min was maintained in the measuring PA cell. The samples were at atmospheric pressure.

Calibration curves for the pulsed, modulated, and chopped systems can be seen in Fig. 2. Note that all PA signals in the figure are microphone signals before amplification. Minimum detectable concentrations (MDCs) are derived by dividing the triplicate of the fluctuation of the background signal (i.e., PA signal at zero ozone concentration) by the slope of the line fitted to the calibration points. The following MDCs are calculated: for the pulsed system 2.8 ppb, while for the modulated and the chopped QCW system 2.9 ppb and 4.4 ppb, respectively.

Field Tests

The frequency quadrupled, quasicontinuous wave Nd:YAG laser–based PA system was tested at the environmental monitoring station of the Lower Tisza Valley Environmental Inspectorate. This station belongs to the Hungarian Air Quality Monitoring Network, it monitors various components such as ozone, NO, NO_2, NO_x, CO, SO_2, PM_{10}, $PM_{2.5}$, BTEX, and meteorological parameters as well, and it continuously supplies concentration data of the measured components (including ozone) to the European Topic Centre on

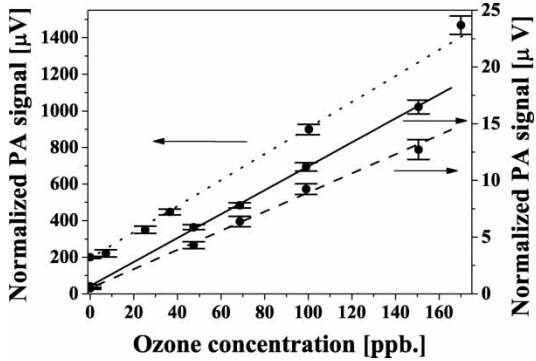

Figure 2. Calibration points—with the corresponding standard deviations of the calibration measurements—for the different PA ozone measuring systems. Also shown are the fitted calibration lines (solid line for chopped QCW, dashed line for modulated QCW, and dotted line for the pulsed system).

Air and Climate Change and to the Topic Centre of European Environment Agency. The PA system was run in parallel with an ozone measuring instrument (49C Thermo Environmental Instruments Inc., Franklin, MA, USA), continuously used at the station. As this latter instrument samples ambient air at zero overpressure, the PA system needed an extra pump (NMP830KVDC, KNF Neuberger, Trenton, NJ, USA) to imbibe the measuring gas sample into the PA cell. This pump was placed after the cell. The flow rate through the PA cell was set to the optimal 200 cm^3/min value with a needle valve between the PA cell and the pump.

During the field test, the modulated QCW system was used, as in this case the use of the chopper could be avoided, thus eliminating a possible source of system failure. Part of the recorded ozone concentration at the environmental monitoring station is shown in Fig. 3. Triangles are for the PA system and circles are for the reference system. Each measurement point is the result of averaging over 30 min. In the insert of Fig. 3, parts of the recordings of the systems are shown in detail. The continuous curve corresponds to the reference instrument, and the dotted curve is the result of the PA system. Both systems used a running average on the raw measurement data, with an averaging time of 1 min. Overall, good agreement between the readings of the reference and PA systems was found. On a short timescale, the PA system seems to have a better time response, but it is not quite clear how strongly this is influenced by the data averaging methods.

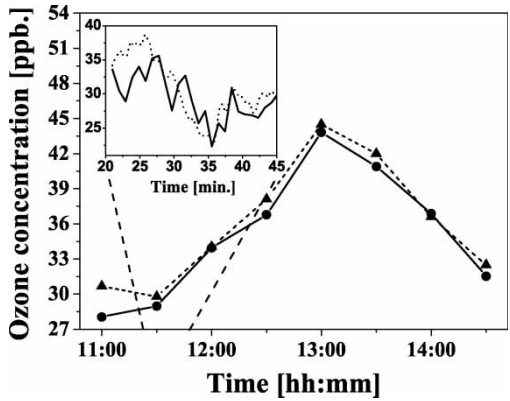

Figure 3. Part of the recorded ozone concentration of ambient air at the environmental monitoring station. Triangles are for the measurements of the modulated QCW PA system, and circles are for the measurements of the reference optical absorption system. Each measurement point is the result of averaging over 30 min. Lines are drawn to guide the eye. In the insert, the recordings of the systems are shown in detail. The continuous curve corresponds to the reference instrument, and the dotted curve is the result of the measurements with the PA system. Both systems used a running average on the raw measurement data, with an averaging time of 1 min.

DISCUSSION

For all the developed systems, a minimum detectable ozone concentration of a few ppb was found. At first sight this looks surprising, as the slope of the calibration curve is much higher for the pulsed system than for the QCW ones. However, the measurement uncertainty is also correspondingly higher for the pulsed system. This uncertainty is not of acoustic origin, because when the laser light was blocked, the background PA noise decreased below 100 nV despite the extremely noisy environment during the operation of the pulsed laser. Uncertainty rather comes from fluctuations in the energy of the 266-nm photons. The most efficient way of reducing this fluctuation of the PA signal was found to be shot-to-shot normalization with the laser energy followed by averaging as described above. In all cases, these detection limits make the systems usable in environmental monitoring applications, however due to its bulkiness, the pulsed system probably has less potential for practical applications.

To compare the different PA techniques, a clear physical basis is needed. This can be introduced in two steps. First, because both pulsed and QCW operation is to be considered, one has to relate the pulse energy and laser power. This can be done by introducing the equivalent laser power (ELP) as proposed in Ref. 15. The ELP is the power level that is necessary to obtain the same PA signal in QCW operation as in pulsed mode with the given pulse energy. The ELP can be obtained by multiplying the width of the acoustic resonance curve of the PA cell (FWHM) by the laser pulse energy. The resonance width can be determined either experimentally or by using the calculation method described in Ref. 16. For our system, using either method it was found to be about 100, thus the ELP for the pulsed arrangement is about 300 mW. In the next step, as a measure of PA signal generation efficiency, one can introduce the effective PA signal (EPAS) as the signal level that is generated in the presence of unit ozone concentration by using unit laser power. It is easy to see that the EPAS can be calculated by dividing the slope of the fitted calibration lines with the laser power. Note that for the chopped QCW system, the laser power is half of the 5.5 mW exiting the nonlinear crystal, as the light is modulated with the chopper before it enters the PA cell. The EPAS was found to be $25\,\mathrm{nV\,ppb^{-1}\,mW^{-1}}$ in the pulsed case, and about $40\,\mathrm{nV\,ppb^{-1}\,mW^{-1}}$ for both QCW systems, respectively. The lower EPAS for the pulsed system can be explained by saturation of the optical absorption. Indeed, for the current experimental arrangement, an energy density of $200\,\mathrm{mJ/cm^2}$ can be estimated inside the PA cell, which is higher than the $75\,\mathrm{mJ/cm^2}$ saturation energy density calculated for ozone at the 266-nm wavelength from the optical absorption coefficient of $300\,\mathrm{cm^{-1}}$.[13] In order to prove the presence of the saturation effect, the PA signal at a fixed ozone concentration was measured as a function of laser power (for the pulsed system it was the ELP). For the pulsed system this curve was nonlinear, which can be seen in Fig. 4 as a decrease in the

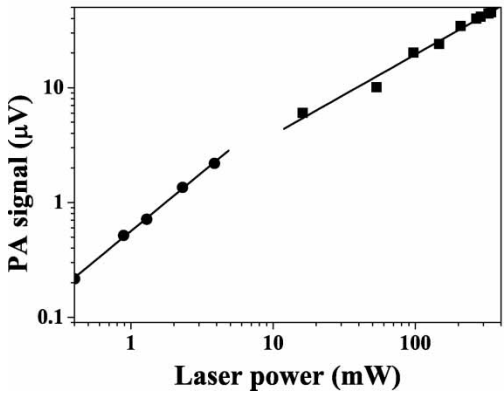

Figure 4. Photoacoustic signal at a fixed ozone concentration as a function of laser power for the modulated QCW (circle) and pulsed (square) system together with fitted lines. Note that for the pulsed system, an effective laser power (i.e., the laser energy multiplied with the FWHM of the acoustic resonance of the PA system) is given.

slope of the line fitted to the laser power-PA signal data point on a log-log scale.

It has to be noted that despite the observed saturation effect, the pulsed system has the potential for detection of ozone with sub-ppb level sensitivity by suppressing the shot-to-shot fluctuation in the UV light energy.

CONCLUSIONS

Two different types of Q-switched Nd:YAG lasers were tested in PA ozone detection. The pulsed system was expected to give sub-ppb sensitivity, while the QCW laser system was intended for field applications. Actually, for the former system, the detection limit was found not to be as low as was expected, due to large signal fluctuations arising from laser energy instabilities, but the latter system was indeed found to be promising in practical applications. To develop this system into a reliable ozone measuring PA instrument with long-term unattended operation, it is necessary to develop a means for ensuring long-term stability of the power of the 266-nm radiation. This work is currently underway in our laboratory.

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