Project Title: Tunable Laser Source Techniques Applied to the Ultraviolet Spectra of Nitrogen Oxides

Project No.: A-1424

Project Director: Mr. James J. Gallagher

Sponsor: National Oceanic and Atmospheric Administration

Effective: April 1, 1972

Estimated to run until: March 31, 1972

Type Agreement: Grant No. No2-145-72-G

Amount: $20,000.00*

*Plus required cost-sharing by Georgia Tech of $1,053

Reports Required:
- Quarterly Progress & Expenditure Statement
- Semi-Annual Fiscal Reports
- Interim Technical Reports
- Final Technical Report

Sponsor Contact Persons:

Technical Matters
Dr. Vernon E. Deel

Administrative Matters
Mr. Boyd L. Green

Project Monitor
National Oceanic & Atmospheric Administration

Contracting Officer
National Oceanic & Atmospheric Administration

Environmental Research Laboratories
Boulder, Colorado 80302

Contracting Office
Boulder, Colorado 80302

Assigned to Special Techniques Division

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GEORGIA INSTITUTE OF TECHNOLOGY
Engineering Experiment Station

PROJECT TERMINATION

Date September 21, 1973

PROJECT TITLE: Tunable Laser Source Techniques Applied to the Ultraviolet Spectra of Nitrogen Oxides

PROJECT NO: A-1424

PROJECT DIRECTOR: Mr. James C. Gallagher

SPONSOR: National Oceanic and Atmospheric Administration

TERMINATION EFFECTIVE: July 31, 1973 (maximum period w/ formal extension)

CHARGES SHOULD CLEAR ACCOUNTING BY: N/A - all funds have been spent.

Grant Closeout Items Remaining: Final Fiscal Report

Final Report of Inventions

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U. S. Department of Commerce  
National Oceanic and Atmospheric Administration  
Environmental Research Laboratories  
Boulder, Colorado 80302  

Subject: Quarterly Progress and Expenditure Report, Grant No.  
N22-145-72(G), "Tunable Laser Source Techniques  
Applied to the Ultraviolet Spectra of Nitrogen Oxides"

Gentlemen:

During the first quarter, the major effort has been in the preparation of the dye laser for accurate, reproducible observations. The existing laser is being reconstructed to provide capabilities which have been shown to be successful in other dye lasers. The flashlamp of the ruby laser which will be employed during this program was destroyed during operation and has been replaced. Some work on the trigger connections is required before the initial doubling and mixing experiments can be performed.

The ultraviolet generation techniques to be employed have been reviewed. These include doubling of the dye laser signal, mixing of the dye and ruby laser outputs and amplification of the dye output before doubling. The latter technique, suggested for consideration by Dr. Derr of NOAA, is difficult to achieve for a dye laser system. However, a recent publication (G. Magyar and H. J. Schneider-Muntau, "Dye Laser Forced Oscillator," Applied Phys. Lett. 20, 406 (1972)) has indicated the possibility of amplifying the dye laser signal, and this method will be considered further.

During the first quarter, a bibliography of the nitrogen oxides has been started in preparation for the spectroscopic observations.
First Quarter Expenditures:

<table>
<thead>
<tr>
<th>Item</th>
<th>Cost</th>
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<tbody>
<tr>
<td>Personnel</td>
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<tr>
<td>Materials:</td>
<td></td>
</tr>
<tr>
<td>1. 1/3 cost of a Xenon Corp. Flash Lamp Model N701A for the dye laser</td>
<td>55.00</td>
</tr>
<tr>
<td>2. Lecture Bottle of Nitric Oxide</td>
<td>4.00</td>
</tr>
</tbody>
</table>

TOTAL $94.24

Respectfully submitted,

J. J. Gallagher
Project Director

Approved:

R. G. Shackelford
Associate Chief,
Special Techniques Division
20 October 1972

U. S. Department of Commerce
National Oceanic and Atmospheric Administration
Environmental Research Laboratories
Boulder, Colorado 80302

Subject: Quarterly Progress and Expenditure Report, Grant No. N22-145-72(G), "Tunable Laser Source Techniques Applied to the Ultraviolet Spectra of Nitrogen Oxides"

Gentlemen:

During the past quarter, Mr. James J. Gallagher visited Dr. Derr, grant monitor, at NOAA to discuss the progress and objectives of the grant. It was agreed that as much effort as possible should be directed toward the following topics:

1. Mixing of a dye laser and a ruby laser;
2. Mixing of two dyes to produce UV and IR radiation;
3. Amplification of the dye followed by harmonic generation into the UV;
4. Properties of nonlinear materials; and
5. Studies of the improvement of the remote sensing receiving system.

The dye laser has been reconstructed so that it can produce more accurate and reproducible results than it previously could. Considerable work has been required for the Korad ruby laser supply. Conversations with the Korad people have indicated that supply changes are necessary to fire the laser by injection triggering. It should be possible during the next few weeks to have this source back in operation.

A Xenon Corporation power supply was received during the past quarter and has been checked out for use in the dye laser. This now provides us with supplies for two dye systems so that both optical mixing and amplification will be possible. A system for amplification of the dye signal has been designed.
Work has started on a determination of the characteristics of the nonlinear materials required for mixing and doubling the dye signals. A survey of all nonlinear materials properties is being made. A report will be prepared during the next quarter on the materials and the requirements for their use in generating ultraviolet radiation.

**Semi-Annual Expenditures:**

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<td>Overhead and Retirement</td>
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<td>Travel</td>
<td>183</td>
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<tr>
<td><strong>TOTAL</strong></td>
<td><strong>$10,275</strong></td>
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</tbody>
</table>

Respectfully submitted,

James J. Gallagher  
Project Director

Approved:

J. W. Dees, Chief  
Special Techniques Division
U. S. Department of Commerce
National Oceanic and Atmospheric Administration
Environmental Research Laboratories
Boulder, Colorado  80302

Subject: Quarterly Progress and Expenditure Report, Grant No. N22-145-72(C), "Tunable Laser Source Techniques Applied to the Ultraviolet Spectra of Nitrogen Oxides"

Gentlemen:

During the past quarter, work continued on the development of the UV source for the spectroscopy of the nitrogen oxides. The dye laser has been operating properly, and a second system has been constructed for amplification of the dye laser output. A set of end windows is needed to complete this system. Considerable work was required to obtain consistent results from the Korad ruby laser, but this is not operating satisfactorily.

A survey of nonlinear materials is nearing completion, and the characteristics for doubling the dye and for mixing it with the ruby laser have been established. Crystals (ADP) are being ordered from Quantum Technology Ltd., for generation of the UV signals. For the harmonic generation, 90° phase matching will be employed so that the crystal will not have to be moved but will be thermally tuned over the range from approximately 5°C to 100°C. This will correspond to a harmonic frequency coverage from approximately .305 nm to .260 nm. A temperature control unit will have to be constructed.

During the next quarter, the UV signals will be generated and used in the spectroscopy of nitric oxide. A McPherson UV spectrometer (available in the Department of Physics) will be employed for the fluorescence observations.

Expenditures through three quarters:

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<thead>
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<th>Item</th>
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<td>Travel</td>
<td>183</td>
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<tr>
<td>Total</td>
<td>$13,799</td>
</tr>
</tbody>
</table>

Respectfully submitted,

James J. Gallagher
Project Director
U. S. Department of Commerce
National Oceanic and Atmospheric Administration
Environmental Research Laboratories
Boulder, Colorado 80302

Subject: Quarterly Progress and Expenditure Report, Grant No. N22-145-72(C), "Tunable Laser Source Techniques Applied to the Ultraviolet Spectra of Nitrogen Oxides"

Gentlemen:

During the last quarter of the grant, work continued on harmonic generation of the dye laser signal. A cell has been completed for use as an amplifier and a thermoelectric temperature controller has been constructed for 90° phase-matching of the ADP doubler.

Improvements in the laser power output are necessary in order to provide consistent harmonic generation. Experimental work has been continued beyond the fourth quarter period, and a final report will be prepared during the first part of July, 1973.

Expenditures through March, 1973 have been:

<table>
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<tr>
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</thead>
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<td>Overhead and Retirement</td>
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<tr>
<td>Materials and Supplies</td>
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<td>Travel</td>
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<tr>
<td><strong>TOTAL</strong></td>
<td><strong>$17,480</strong></td>
</tr>
</tbody>
</table>

Respectively submitted,

James J. Gallagher
Project Director

Approved:

J. W. Dees, Chief
Special Techniques Division
TUNABLE LASER SOURCE TECHNIQUES APPLIED TO THE ULTRAVIOLET SPECTRA OF NITROGEN OXIDES

By

James J. Gallagher
Engineering Experiment Station
Georgia Institute of Technology
Atlanta, Georgia 30332

FINAL REPORT

Period Covered: 1 April 1972 through 30 June 1973

23 August 1973

Prepared for

U. S. Department of Commerce
National Oceanic and Atmospheric Administration
Environmental Research Laboratories
Boulder, Colorado 80302
ABSTRACT

Investigations have been performed on techniques for the generation of tunable ultraviolet radiation for fluorescent spectroscopy of nitrogen oxide molecules. Dye lasers and the improvement of their power output have been studied. Harmonic generation and nonlinear optical mixing schemes have been considered. Amplification of the dye laser output and construction of various flashlamp configurations have been studied. The features of nitrogen oxide spectra important to fluorescence observations have been outlined.
I. INTRODUCTION

The nitrogen oxide molecules have electronic transitions which lie in the ultraviolet spectral region, which has thus far been unaccessible to suitable laser sources for absorption or fluorescence experiments. The investigations performed under this grant have been concerned with the development of tunable sources in the spectral region from approximately 0.2000 μm to 0.3500 μm. Since no tunable lasers exist in this region, the goal will have to be achieved by either harmonic generation of dye lasers or by mixing of the dye laser with another fixed frequency laser.

Considerable effort was expended during the grant to obtain sufficient power for the nonlinear optical interactions. Improvement of existing dye lasers, amplification techniques and flashlamp construction have been studied. At the end of the grant, Dr. Derr, NOAA technical monitor for the grant, indicated that recent success in pumping a dye laser with a helical flashlamp was of interest, and an attempt was made to operate such a system. Damage to the flashlamp has delayed this particular investigation, but the effort will continue under different sponsorship when a new lamp is obtained.

The spectral region from approximately 0.2200 μm to 0.3000 μm is important for the β and γ bands of NO. In order to cover this region, different nonlinear optical techniques must be employed. It will be shown in Section III that phase matching for harmonic generation in ADP and KDP, the only available crystals for UV generation, becomes impractical for fundamental wavelengths much below 0.500 μm. Various optical mixing schemes have been considered; however, similar limitations apply to these techniques.

During the course of this grant, related publications have appeared or come to our attention. Employing an intracavity ADP crystal, Wallace [1] generated tunable UV radiation by two methods: (1) doubling the output of a dye laser, and (2) summing the dye with an Nd:YAG pump laser. The spectral range covered was 0.26 - 0.31 μm. Approximately 32 mW average power was obtained. In addition, an external 90° phase matched, temperature tuned ADP crystal was used for doubling and summing. The temperature control of the doubler dictated the shortest wavelength achieved. This work is the basis for a commercial apparatus which has become available [2].
Prior to Wallace's work, Huth, et al. [3] had frequency doubled a flashlamp pumped Rhodamine 6G laser with a KDP crystal. The spectral range covered by the second harmonic was from 0.290 \( \mu \text{m} \) to 0.300 \( \mu \text{m} \).

More recently, 90° phase-matched temperature tuning has been considered in detail for the KDP isomorphs [4,5]. A second harmonic of the 0.4965 \( \mu \text{m} \) line of the argon laser has been obtained by 90° phase matching in ADP, but this has required temperatures of -93.2°C [6]. It is seen that the lower wavelength limits for phase-matched second-harmonic generation (SHG) in ADP is in the range of 0.490 \( \mu \text{m} \) for the fundamental wavelength and that this is dictated by the Curie temperature (172°K) for the crystal. Mixing schemes have similar limits in getting below 0.245 \( \mu \text{m} \) in the UV. Recently, the mixing of a ruby laser and a dye laser has been reported [7], but no details of the experiments have been reported.

On the basis of the existing nonlinear materials, the optical spectra of the nitrogen oxide molecules can be studied at wavelengths longer than 0.245 \( \mu \text{m} \), but new materials and/or techniques will have to be developed to operate at wavelengths below this limit.
inches long and has an O.D. of approximately 5/8 inch with a bore on the order of 0.54 inches. This cell is similar to one described by Dr. Derr in a personal communication. Damage to the helical flashlamp during the initial investigations with this system has delayed operation. While the helical lamp operates at 5 kV, very large energy is available from the supply. Approximately 4250 joules constitute the input to the flashlamp at 5 kV.

(3) A Candela CL-100E Coaxial Flashlamp and dye cell have been obtained to provide an increased dye output. These lamps, capable of operating at 100 joule input, will be operated with approximately 55 joules input, which is far greater than the energies currently being employed.

(4) Flashlamps are currently being constructed. These are of the coaxial type, similar to those of Sorokin, et al. [10]. Both helical and linear lamps [11] are being constructed for this work.

No spectral narrowing methods other than the use of the grating have been employed for this work. The spectral coverage of the Rhodamine 6G in a water solution with 4% Ammonyx LO was checked with a Jarrell Ash ½ meter spectrometer and found to extend from 0.5797 μm to 0.6291 μm with the supply operating at 12 kV. Further narrowing will be desired when observing NO in the ultraviolet, since the Doppler broadened line is approximately 0.05 cm⁻¹ or 2.7 x 10⁻³ Å at 0.2400 μm.
\[
\sin^2 \theta_m = \frac{[n_o(w)]^{-2} - [n_o(2w)]^{-2}}{[n_e(2w)]^{-2} - [n_o(2w)]^{-2}} \tag{1}
\]

Type II phase matching has a component of the input wave as an o-ray and a component as an e-ray. The output is an e-ray. The phase matching condition is then

\[
\left[ \frac{\cos^2 \theta_m}{[n_o(2w)]^2} + \frac{\sin^2 \theta_m}{[n_e(2w)]^2} \right]^{-\frac{1}{2}} = \left\{ n_o(w) + \left[ \frac{\cos^2 \theta_m}{[n_o(w)]^2} + \frac{\sin^2 \theta_m}{[n_e(w)]^2} \right]^{-\frac{1}{2}} \right\} \tag{2}
\]

It is found that the shortest wavelength generation in the ultraviolet can be achieved by 90° phase-matching with the temperature of the nonlinear crystal adjusted so that the refractive index of the fundamental equals that of the second harmonic. The 90° phase-matching conditions are then

Type I: \( n_e(2w) = n_o(w) \) \tag{3}

with the phase matching temperature given by [11]

\[
T_m = T_o + \frac{n_o(w) - n_e(2w)}{\frac{dn_e(2w)}{dT} - \frac{dn_o(w)}{dT}} \tag{4}
\]

Type II: \( n_e(2w) = \frac{1}{2}[n_o(w) + n_e(w)] \) \tag{5}

and

\[
T_m = T_o + \frac{\frac{1}{2}[n_o(w) + n_e(w)] - n_e(2w)}{\frac{dn_e(2w)}{dT} - \frac{dn_o(w)}{dT} - \frac{1}{2} \frac{d}{dT} [n_o(w) + n_e(w)]} \tag{6}
\]
It can be seen from a comparison of the indices of refraction that ADP with Type I 90° phase matching provides the optimum SHG into the UV. The indices of refraction have been determined for discrete wavelengths to 0.2000 μm [12] and can be calculated for any desired wavelength from a Sellmeier equation. The coefficients of this equation have been given by Zernike [12], and the indices of refraction are given for ADP as

\[ n_o^2 = 2.302484 + \frac{1.117089 \times 10^{-10} \nu^2}{[1 - (\nu^2/7.605372 \times 10^9)]} + \frac{3.751806 \times 10^6}{(2.5 \times 10^{-5} - \nu^2)} \]  

and

\[ n_e^2 = 2.163077 + \frac{9.670312 \times 10^{-11} \nu^2}{[1 - (\nu^2/7.785289 \times 10^9)]} + \frac{1.451540 \times 10^6}{(2.5 \times 10^{-5} - \nu^2)} \]  

where \( \nu = 1/\lambda \) in cm\(^{-1}\).

The change in index of refraction for ADP is given by [13]

\[ \Delta n_o = (n_o^2 - 3.0297 n_o + 2.300) \times (0.713 \times 10^{-2}) \times (298 - T) \]  

\[ \Delta n_e = (n_e^2) (0.675 \times 10^{-6}) \times (298 - T) \]

where the temperature \( T \) is given in degrees Kelvin.

Similar expressions exist for KDP, but ADP permits phase-matching slightly further into the UV. For mixing with ADP, expressions similar to those for harmonic generation are used. In the summing of two signals at frequencies \( \omega_1 \) and \( \omega_2 \) to generate the signal at frequency \( \omega_3 \), the following relations hold: \( \omega_1 + \omega_2 = \omega_3 \).
Type I Phase-matching -

\[
\left[ \left( \frac{\cos \theta_m}{n_o(w_3)} \right)^2 + \left( \frac{\sin \theta_m}{n_e(w_3)} \right)^2 \right]^{\frac{1}{2}} = \frac{1}{2} \left[ n_o(w_1) + n_o(w_2) \right]
\]

(11)

where the input signals at \( w_1 \) and \( w_2 \) are \( o \)-rays, and the generated signal at \( w_3 \) is an \( e \)-ray.

Type II Phase-matching -

\[
\left[ \left( \frac{\cos \theta_m}{n_o(w_3)} \right)^2 + \left( \frac{\sin \theta_m}{n_e(w_3)} \right)^2 \right]^{\frac{1}{2}} = \frac{1}{2} \left\{ \left[ \left( \frac{\cos \theta_m}{n_o(w_1)} \right)^2 + \left( \frac{\sin \theta_m}{n_e(w_1)} \right)^2 \right]^{\frac{1}{2}} \right\} + n_o(w_2)
\]

(12)

where \( E_3 \) and \( E_2 \) (or \( E_1 \)) are \( e \)-rays, and \( E_1 \) (or \( E_2 \)) is an \( o \)-ray.

For \( 90^\circ \) phase-matching, these relations reduce to:

Type I \[ n_e(w_3) = \frac{1}{2} \left[ n_o(w_1) + n_o(w_2) \right] \]  

(13)

Type II \[ n_e(w_3) = \frac{1}{2} \left[ n_o(w_1) + n_o(w_2) \right] \]  

(14)

with the phase-matching temperature given for Type I conditions by

\[
T_m = T_o + \frac{\frac{1}{2} \left[ n_o(w_1) + n_o(w_2) \right] - n_e(w_3)}{\frac{d n_e}{dT}(w_3) - \frac{1}{2} \frac{d}{dT} \left[ n_o(w_1) + n_o(w_2) \right]}
\]

(15)

A few examples will give an indication of the short wavelength limit of UV generation by nonlinear optical schemes. For SHG by \( 90^\circ \) phase-matching and temperature tuning, the equations (3), (4), (7), (8), (9) and (10) show that the limit is \( \lambda_1 = 5018\text{Å} \) for the fundamental to generate
of reduced lithium niobate have been employed to generate tunable far-IR radiation by difference frequency mixing of dye lasers [17]. While phase-matching techniques are not employed, two nonlinearities that are not present in transparent materials are used. These nonlinearities are the change in dipole moment of the absorbing centers under optical excitation and the polarization that accompanies the subsequent thermalization of the excitation. The magnitudes of these effects are proportional to the optical absorption coefficient. These effects should be studied for applications in the UV for \( \lambda < 250 \text{ nm} \), for, if there's one thing that this wavelength region doesn't lack, it's good absorbing materials.

In the harmonic generation which has been considered thus far, only ADP has been employed. Concurrently, work has been performed on improving the dye lasers. A comparison has been made of the transmission of two ADP crystals. One of these is the crystal employed for doubling the ruby laser while the second crystal is one purchased from Quantum Technology. The latter crystal was 80-90% transmitting out to 2000Å, while the Korad crystal was approximately 60% transmitting from 2000-3000Å. A small chamber, capable of being evacuated or flushed with dry nitrogen, was constructed for holding the nonlinear crystal. The crystal is mounted on a Borg-Warner thermoelectric cooler. The circuit for the cooler is arranged so that the crystal can be cooled to approximately \(-58^\circ\text{C}\) or heated to slightly less than \(100^\circ\text{C}\). An EMI photomultiplier Type 9781 with an S-81 surface, capable of detection to 2000Å, is employed with a Jarrell-Ash \( \frac{1}{2} \) meter spectrometer to detect the UV output. While harmonic generation of both the dye laser and the ruby laser have been observed, improvements in the lasers and filtering techniques are necessary for the spectroscopic observations.
V. REFERENCES

2. Chromatix Model 1050 UV-Vis Dye Laser.
15. J. F. Young, A. H. Kung, G. C. Bjorklund, and S. E. Harris, CLEA Proceedings, Paper 17.1, p. 82 (May 1973);
   A. H. Kung, et al., Appl. Phys. Ltrs. 22, 301 (1973);
   S. E. Harris, R. L. Byer, R. L. Herbst, R. B. Miles, J. F. Young, "Tunable Optical Sources," Final Report, Microwave Laboratory, Stanford University, California, June 30, 1972, AD-748-849;
   A. H. Kung, J. F. Young, G. C. Bjorklund, S. E. Harris, R. B. Miles, "Research Studies on Nonlinear Optical Processes in Metal Vapors," Annual Report, Microwave Laboratory, Stanford University, California, December, 1972, AD-754-096;


