

Final Technical Report

National Science Foundation
Grant CHE-8604471

"Characterization of Small Metal
Clusters and Their Unique Oxidation Processes"

James L. Gole

School of Physics
Georgia Institute of Technology

Table of Contents

	page
1. Summary of Research Effort.	1
2. Publications.	1
3. Abstracts of Published Journal Articles	4
4. Seminars and Invited Talks on NSF Sponsored Research.	11
5. Metal Clusters and Their Unique Reaction Dynamics (a summary of significant aspects of the research effort - national press recognition as presented to K. H. Houk, March, 1989)	13

Summary of Research Effort

Our research effort under NSF Grant CHE-8604471 has focused on the experimental and theoretical treatment of small metal clusters and their ions and the unique oxidation processes which they undergo. Included in this effort have been several breakthroughs.

We have demonstrated the first chemically pumped continuous laser amplifier in the visible spectral region, based on the characterization of the $\text{Na}_3 + \text{X}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) reactions. We have developed a source configuration which has allowed the first analysis of middle transition metal cluster (Ni_3) quantal structure. We are completing the first phases of a group of studies in which we have observed and analyzed the optical signatures for the products of metal cluster oxidation, this work yielding important information on the kinetically controlled formation of the asymmetrical cluster oxides M_2O and M_xO ($x \geq 3$). It is significant that the metal cluster oxides we generate represent the nonsymmetrical isomers, M_xO , rather than those compounds which might be synthesized through thermochemical means. The study of the unsymmetrical isomers provides a closer parallel to the nature of reactions on a metallic surface and the catalytic action of such surfaces and complements the ongoing studies of neutral and ionic cluster reactivity now underway in a number of research groups. In addition, we initiated studies whose focus has been on the formation of metal based CO and CO_2 complexes and the determination of the corresponding metal-ligand binding energies. These species can serve as prototype models for CO chemisorption on metal surfaces. We have also completed a theoretical study of the proton affinities of Li_2 , Na_2 , LiH , and NaH and the alkali cation affinities of N_2 , CO, and H_2 . These studies represent the lead to the future study of the Li_2H^+ and Na_2H^+ cations using laser vaporization plasma spectroscopy.

Finally, in developing the technique of Electric Field Enhanced Laser Induced Plasma Spectroscopy we have initiated the study of the internal mode structure and dynamics of small copper, aluminum, carbon and silicon metal and metalloid clusters, their ions and the hydrides of these metal clusters and their ions.

Publications

"Formation and Oxidation of Intense Metal Cluster Beams and Flows", in Proceedings of the International Workshop on Ionized Cluster Beam Techniques (ICBT) '86, Tokyo and Kyoto, Japan, pg. 85.

"Self-Flushing Optical Window to Prevent Collection of Condensates", J. L. Gole, W. H. Crumley, Rev. Sci. Instruments, 57, 1692 (1986).

"Bound-Free Transitions in Molecular Metal Trimers", in Proceedings of the International Laser Science Conference, American Institute of Physics Conference Proceedings No. 146, Advances in Laser Science - page 522 (1986).

"Potential Probes of Metal Cluster Oxide Quantum Levels - Optical Signatures for the Oxidation of Small Metal Clusters M_x ($\text{M} = \text{Cu}, \text{Ag}, \text{Mn}, \text{B}$)", J. L. Gole, R. Woodward, P. N. Le, and M. Temmen, Jour. Phys. Chem. Cluster Symposium Issue 91, 2637 (1987).

- "Quantum Level Probes of Small Metal Clusters and Their Oxidations", American Institute of Physics Conference Proceedings, No. 160, Advances in Laser Science II - Optical Science and Engineering Series 8, pg. 439.
- "A Chemical Process Producing a Continuous Laser Amplifier in the Visible Region", J. L. Gole, S. H. Cobb and R. Woodward, Chem. Phys. Lett. 143, 205 (1988).
- "The Lithium and Sodium Cation Affinities of H_2 , N_2 and CO ", J. L. Gole, D. A. Dixon, and A. Kormornicki, J. Phys. Chem. 92, 1378 (1988).
- "The Proton Affinities of LiH , NaH , Li_2 , and Na_2 ", J. L. Gole, D. A. Dixon, and A. Kormornicki, J. Phys. Chem. 92, 2134 (1988).
- "Oxidation of Small Boron Clusters - Formation of and Chemiluminescence from BBO ", J. L. Gole, T. C. Devore and R. Woodward, J. Phys. Chem. 92, 6919 (1988).
- "Gas Phase Laser Induced Excitation Spectrum of Nickel Trimer", J. L. Gole, R. W. Woodward and S. H. Cobb, J. Phys. Chem. 92, 1404 (1988).
- "Formation and Oxidation of Metal Based CO and CO_2 Complexes - Characterization of $Al(CO)_x$ and $Al(CO_2)_x$ and Their Oxidation", J. L. Gole, M. McQuaid, and J. R. Woodward, J. Phys. Chem. Letts. 92, 252 (1988).
- "Trends in the Optical Signatures for Transition Metal Oxide Carbonyl Complexes - Evaluation of Transition Metal Carbonyl $M(CO)_x$ ($x = 1,2$) Binding Energies", J. L. Gole, M. McQuaid, J. Am. Chem. Soc., 110, 5280 (1988).
- "Formation of Electronically Excited Mn_xO from the Oxidation of Small Manganese Clusters", J. L. Gole, T. C. Devore and J. R. Woodward, Journal of Physical Chemistry, 93, 4920 (1989).
- "Formation of Electronically Excited Ag_xO from the Oxidation of Small Silver Clusters", J. L. Gole, R. Woodward, P. N. Le, T. C. Devore, and D. A. Dixon, Jour. Phys. Chem. in press.
- "Formation and Characterization of a Low-Lying Electronic State of the Alkali Monoxides $LiO...CsO$ at the Fringes of the Visible Region", J. L. Gole, R. Woodward and J. S. Hayden, Chem. Phys., 134, 395 (1989).
- "Chromium Cluster Fluorination - Three New States of CrF and the Observation of the First Cr_xF Emission Spectra", T. C. Devore, M. McQuaid, and J. L. Gole, High Temperature Science, in press.
- "Continuous Chemical Amplification of Single and Multimode Lasers in the Visible Region", with S. H. Cobb and J. R. Woodward, Chem. Phys. Lett., 156, 197 (1989).
- "Electric Field Enhanced Laser Induced Plasma Spectroscopy of Jet Cooled Metal Clusters and Their Hydrides", with K. X. He, M. Diestler, M. Xu, E. Daykin, and K. Everett, Bull. Am. Phys. Soc.

"Formation of the Low-Lying Electronic States of CrO in Highly Exothermic Reaction Oxidation, - Assessment of New States and Resolution of Previous Observations", with T. C. Devore, Chemical Physics, 133, 95 (1989).

"Electric Field Enhanced Laser Induced Plasma Spectroscopy of Jet Cooled Metal Clusters and Their Ions", with K. X. He, M. Diestler, M. Xu, and E. Daykin, Chemical Physics Letters, submitted.

"Stability and Oxidation of Metal Based CO and CO₂ Complexes", with M. J. McQuaid, Proceedings of the Fourth International Laser Science Conference, in press.

"Continuous Chemical Laser Amplifiers in the Visible Region", with S. H. Cobb and J. R. Woodward, Proceedings of the Fourth International Laser Science Conference, in press.

"Oxidation of Small Metal Clusters", with T. C. Devore, Proceedings of the Sixth International Conference on High Temperature Materials, in press.

"Spectroscopy of the AlAr Van der Waals Complex: Rotationally Resolved $B^2\Sigma^+ \leftarrow X^2\Pi_{1/2}$ Electronic Transitions", with M. McQuaid and M. C. Heaven, J. Chem. Phys., in press.

SELF-FLUSHING OPTICAL WINDOW TO PREVENT COLLECTION OF CONDENSATES

W. H. Crumley and J. L. Gole

As an aid to the characterization of nominally condensible and/or high-temperature molecules using optical techniques, a self-flushing optical window operating at room temperature and requiring no external heating has been designed to prevent the collection of these condensates. The optical design allows the unobstructed transmittance of light into and out of several devices to which it is readily adopted.

POTENTIAL PROBES OF METAL CLUSTER OXIDE QUANTUM LEVELS. OPTICAL SIGNATURES FOR THE OXIDATION OF SMALL METAL CLUSTERS M_x ($M = \text{Cu, Ag, B, Mn}$)

R. Woodward, P. N. Le, M. Temmen, and J. L. Gole

A source configuration which lies intermediate to a low-pressure effusing molecular beam and a high-pressure flow device is used to generate large concentrations of small metal clusters in a highly oxidizing environment. Clusters are formed from a high metal flux source ($K_{\text{Knudsen}} < 1$), which creates the seed for the initial phases of a cluster-forming environment, and are further agglomerated in a controlled argon or helium flow at room to liquid nitrogen temperature. The high-flux noneffusive source has been combined with techniques which have proven valuable in studying chemiluminescent processes across a wide pressure range to probe the chemiluminescent emission from several processes including the oxidation of small copper ($\text{Cu}_x + \text{O}_3$), silver ($\text{Ag}_x + \text{O}_3$), boron ($\text{B}_x + \text{NO}_2, \text{N}_2\text{O}$), group IVA (group 14), and early transition-metal clusters. From these studies we have obtained the first quantal information on the energy levels and optical signatures of several metal cluster oxides, $M_n\text{O}_y$. The present study outlines the potential for chemiluminescent probes of metal cluster oxide quantum levels, not only within themselves but as a means of suggesting future laser fluorescent probes of the metal cluster oxides.

A CHEMICAL PROCESS PRODUCING A CONTINUOUS LASER AMPLIFIER IN THE VISIBLE REGION

S. H. Cobb, R. Woodward and James L. Gole

In a study of the reaction dynamics of the $\text{Na}_3\text{-X}$ (Cl, Br, I) metatheses, Na_2 is formed in several electronic states, the fluorescence from these states resembling in some respects that characteristic of optically pumped alkali dimer lasers. Optical gain through stimulated emission demonstrates population inversion involving several excited state levels of Na_2 and hence an amplifying medium for a visible chemical laser. A maximum laser gain of 1% of the input laser power has been observed at 5270 \AA , corresponding to a gain coefficient of $\approx 2 \times 10^{-3} \text{ cm}^{-1}$. An explanation is provided for this efficient inversion process and comparisons are made with optically pumped laser systems.

LITHIUM AND SODIUM CATION AFFINITIES OF H₂, N₂, AND CO

David A. Dixon, James L. Gole, and Andrew Komornicki

The Li⁺ and Na⁺ affinities of H₂, N₂, and CO have been calculated by ab initio molecular orbital theory with extended basis sets. Geometries were gradient optimized at the self-consistent field (SCF) level. Force fields were calculated at the SCF level at stationary points as were correlation corrections at the CI(SD) level with a correction for higher order excitations where appropriate. The optimum geometries are C_{2v} (bent) for MH₂⁺ and C_{∞v} (linear) for MCO⁺, MOC⁺, and MN₂⁺. The Li⁺ affinities (ΔH at 300 K) for H₂, CO (at O), CO (at C), and N₂ are 4.8, 12.0, 14.6, and 11.8 kcal/mol, respectively, at the correlated level. The Na⁺ affinities (ΔH at 300 K) for H₂, CO (at O), CO (at C), and N₂ are 2.8, 7.6, 9.6, and 7.4 kcal/mol, respectively, at the correlated level.

ABSOLUTE PROTON AFFINITIES OF Li₂, Na₂, AND NaH

David A. Dixon, James L. Gole, and Andrew Komornicki

The proton affinities of LiH, NaH, Li₂, and Na₂ have been calculated by ab initio molecular orbital theory with extended basis sets. Geometries were gradient optimized and force fields were calculated at the SCF level. Correlation corrections were calculated at the CI-SD level for the valence electrons. The proton affinities are calculated to be 244.2, 261.8, 277.8, and 274.1 kcal/mol for LiH, NaH, Li₂ and Na₂. The Li⁺ affinity of LiH is calculated to be 56.4 kcal/mol, and the Na⁺ affinity of NaH is calculated to be 49.7 kcal/mol.

OXIDATION OF SMALL BORON AGGLOMERATES: FORMATION OF AND CHEMILUMINESCENT EMISSION FROM BBO

T. C. Devore, J. R. Woodward, and J. L. Gole

A source configuration that lies intermediate to a low-pressure effusing molecular beam and a high-pressure flow device is used to generate boron cluster molecules in a highly oxidizing environment. Using this source operating in an NO₂ or N₂O oxidative environment, we generate a chemiluminescent emission spectrum which we attribute to the asymmetric BBO molecule. The observed spectrum is characterized by a strong Δv = 0, Δv = 40 cm⁻¹ sequence grouping and a weaker Δv = +1 sequence (Δv = 40 cm⁻¹), 440 cm⁻¹ to higher energy. A second sequence with Δv ~ 142 cm⁻¹ is also observed. Combining the 440-cm⁻¹ upper-state frequency with the 142-cm⁻¹ sequence structure implies a lower-state frequency of ~582 cm⁻¹ for the B-B stretch, consistent with ab initio calculation.

GAS-PHASE LASER-INDUCED EXCITATION SPECTRUM OF NICKEL TRIMER

J. R. Woodward, S. H. Cobb, and J. L. Gole

The first gas-phase nickel trimer laser-induced excitation spectrum has been generated from the supersonic expansion of pure nickel vapor. The spectrum, which correlates well with that observed in matrix isolation

studies, appears to be dominated by a combination of symmetric stretch and bending mode frequencies. On the basis of the results obtained we suggest an approach to overcome the substantial loss mechanisms which plague metal cluster spectroscopy and evaluate ground-state transition-metal cluster quantal structure.

FORMATION AND OXIDATION OF METAL-BASED CO AND CO₂ COMPLEXES: CHARACTERIZATION OF Al(CO)_x AND Al(CO₂)_x AND THEIR OXIDATION

M. McQuaid, J. R. Woodward, and J. L. Gole*

In a comparative study, aluminum atoms entrained in argon, CO, and CO₂ are oxidized with ozone to inspect the nature of aluminum complexation with CO and CO₂ to form Al(CO)_x (x = 1,2) and AlCO₂ adducts. The optical signatures corresponding to the chemiluminescent oxidation of these complexes with ozone to form the AlO B²Σ⁺ state or, in the case of CO₂, a polyatomic complex are compared to that AlO B²Σ⁺ emission associated with the chemiluminescent oxidation of nonbonded aluminum atoms in argon. We (1) establish a method for evaluating M(CO)_x binding energies and (2) observe the optical signature for a potentially long-lived (~10⁻⁷s) metal oxide-carbon dioxide solvation complex formed in metal-CO₂ complex oxidation. From a comparison of these studies, with results obtained for Al-N₂O oxidation, we estimate a lower bound to the total Al(CO)₂ binding energy (to Al + 2CO) of ~0.7 eV. The current study in conjunction with parallel efforts involving the transition metals suggests a method for studying the spectra of MCO, M(CO)₂, and M-CO₂ complexes.

TRENDS IN THE OPTICAL SIGNATURES FOR TRANSITION-METAL OXIDE CARBONYL COMPLEXES. EVALUATION OF TRANSITION-METAL CARBONYL, M(CO)_x, BINDING ENERGIES

M. J. McQuaid, K. Morris, and J. L. Gole*

Transition-metal atoms entrained in argon, helium, and CO are oxidized with ozone (O₃) and nitrogen dioxide (NO₂) to study the nature of the metal atom complexation with CO. We establish a method for evaluating M-CO binding energies through comparison of the chemiluminescent emission from the oxidation of argon- and CO-entrained transition-metal atoms. These studies have thus far yielded E_{binding}(Ti(CO)_x) ≈ 1.75 eV and E_{binding}(NiCO) ≈ 1.10 eV, the latter in excellent agreement with previous experimental and theoretical evaluations of the Ni-CO bond energy. We identify the optical signatures for transition-metal oxide carbonyl (MOCO) complexes formed in the oxidation of M(CO) complexes. We outline trends in the nature of the observed metal oxide complex emissions. The current study suggests a method for obtaining the spectra of transition-metal carbonyl (M(CO)_x, x = 1,2) complexes.

FORMATION OF ELECTRONICALLY EXCITED Mn_xO FROM THE OXIDATION OF SMALL MANGANESE CLUSTERS

T. C. Devore, J. R. Woodward, and J. L. Gole

The chemiluminescent reactions of manganese atoms and clusters with ozone have been studied under multiple collision conditions. Manganese atoms entrained in room temperature argon or helium react with ozone to form the

lowest-lying $\text{MnO}^* \text{A}^7\Sigma^+$ excited electronic state ($\text{Mn} + \text{O}_3 + \text{Ar}(\text{He}) \rightarrow \text{MnO}^* (\text{A}^7\Sigma^+) + \text{O}_2 + \text{Ar}(\text{He})$) producing a strong chemiluminescent signal corresponding to the $\text{MnO} \text{A}^7\Sigma^+ - \text{X}^7\Sigma^+$ band system. A high flux of manganese vapor is entrained in LN_2 cooled argon to induce clustering. This entrained mixture subsequently reacts with ozone to produce a new complex emission system (which accompanies the $\text{MnO} \text{A-X}$ system) containing at least 72 bands and extending from 720 to 970 nm. The new system which is not present unless the carrier gas is cooled increases precipitously with entrainment gas cooling and increased metal flux. The observed bands are fit within experimental error by the expression

$$\nu_{v'_1, v''_1, v'_3, v''_3} = 12512 + 600v'_1 - 534v''_1 + 360v'_3 - 306v''_3$$

where all the values are in cm^{-1} . The ground state spacing of 306 cm^{-1} is assigned as an Mn-Mn stretch. The 534 cm^{-1} spacing is assigned to an MnO stretch and the emitting molecule is believed to be the asymmetrical Mn-Mn-O isomer.

The Mn-Mn stretch frequency is in excellent agreement with the frequency estimated for Mn_2^+ by averaging the derived force constants for Mn_2 and Cr_2 . The MnO stretching frequency is considerably lower than the 840 cm^{-1} diatomic frequency, lying intermediate to those of KO (384 cm^{-1}) and CaO (733 cm^{-1}). This suggests that the bonding in this molecule is similar to the bonding in the alkali oxides and that it may reasonably be represented as $(\text{Mn-Mn})^+\text{O}^-$.

FORMATION OF ELECTRONICALLY EXCITED Ag_xO FROM THE OXIDATION OF SMALL SILVER CLUSTERS

T. C. Devore, J. R. Woodward, P. N. Le, D. A. Dixon, and J. L. Gole

The chemiluminescent reactions of silver clusters, M_n , $n \geq 3$, with ozone have been studied under multiple collision conditions. As a function of variations in the silver flux, a minimum of five distinct electronic emissions associated with AgO , $\text{Ag}_x\text{O}(x \geq 2)$, and Ag_2 are observed as well as features which are tentatively associated with the higher silver cluster oxides. The energetics of the observed spectral features combined with supplementary thermodynamic and kinetic information demonstrate that it is unlikely that electronically excited products with enough energy to account for the observed chemiluminescence can be produced through the reaction of either Ag or Ag_2 with O_3 . The smallest cluster whose reactions can readily yield the observed AgO emission features is the trimer. The formation of Ag_2O^* can also be achieved through reaction of the trimer, however, it may better be accounted for via the reaction of higher clusters. At moderate silver fluxes, the observed chemiluminescence is dominated by the $\text{AgO} \text{A}^2\Pi - \text{X}^2\Pi$ ($400\text{-}420\text{nm}$) and $\text{B}^2\Pi - \text{X}^2\Pi$ ($320\text{-}370\text{nm}$) emission features. At higher silver fluxes, leading to greater agglomeration, both the $\text{AgO} \text{A-X}$ and B-X emissions are quenched and the spectrum is dominated by a combination of $\text{Ag}_x\text{O}(x \geq 2)$ and Ag_2 emission features extending from 420 to 700 nm. At even higher silver flux further spectral features at $> 680 \text{ nm}$ emerge.

The chemiluminescent spectrum between 500 and 700 nm has been found to contain two distinct emission band regions which have been assigned as the A-X and B-X band systems of Ag_2O . The A-X transition which onsets at $\sim 630 \text{ nm}$ is well fit by the expression

$$\nu(\text{cm}^{-1}) = 15670 - 165v''_2 + (0.4)v''_2{}^2.$$

The B-X transition which originates at 506 nm is well fit by the expression

$$\nu(\text{cm}^{-1})_{v''_1, v''_2, v''_3} = 19766 - 442v''_1 - 165v''_2 - 256v''_3 + 6v''_1^2 + 6(v''_1)(v''_3) = 25(v''_1)(v''_2)$$

The observed frequencies are consistent with a non-linear Ag-Ag-O structure, emission from the asymmetric cluster oxides characterizing these kinetically controlled oxidation experiments in contrast to the thermodynamically more stable symmetric species.

FORMATION AND CHARACTERIZATION OF A LOW-LYING ELECTRONIC STATE OF THE ALKALI MONOXIDES LiO...CsO IN THE RED AND NEAR INFRARED

J. R. Woodward, J. S. Hayden and J. L. Gole

In studying a variety of highly exothermic alkali oxidation chemiluminescent processes, a significant body of evidence has been obtained to indicate that the alkali monoxides LiO, NaO, KO, RbO, and CsO possess a weakly bound, low-lying predominantly covalent excited electronic state thought to be of 2π symmetry ($B^2\pi$). The emission from this state for the heavier alkali oxides lies at the fringes of the visible region whereas the LiO emission system extends through the entire visible range to the near infrared. Alkali atoms react with ozone (O_3) and nitrous oxide (N_2O) under both single collision beam-gas and multiple collision conditions to yield the chemiluminescent spectra ascribed to the alkali monoxides. Under single collision conditions, the observed emission spectra resulting from an oxidation process first order in metal and first order in oxidant are virtually continuous. The single collision studies are extended in a controlled manner to higher pressures ranging from 0.15 to 1 Torr in order to study the internal relaxation and rapid intramolecular energy transfer characteristic of the metal monoxide. Partially rotationally relaxed spectra obtained for LiO, NaO, and KO demonstrate considerable structure associated predominantly with the vibrational levels of the ground and very low-lying ionic states of the alkali oxides. Temperature dependence studies (T_{beam}) under single collision conditions demonstrate that the O_3 reactions proceed with much lower activation energy for excited state formation versus the N_2O reactions. Through energy conservation, the bond energies for LiO, NaO, KO, and CsO are extracted. While those bond energies determined for NaO, KO, and CsO are in good agreement with previous workers, the determined bond energy for LiO is notably higher than that determined mass spectrometrically. This study correlates well with the recent evaluation of M_2+O_2 alkali oxidation processes where weak emission from an MO_2 ($M=\text{Na...Cs}$) species appears to be observed. The significance of the low-lying alkali oxide state as it pertains to the detection of the alkali oxides in combustion streams is considered.

FLUORINATION OF COMPLEXED CHROMIUM ATOMS AND MOLECULES - THREE NEW STATES OF CrF AND THE POSSIBLE OBSERVATION OF Cr_xF EMISSION SPECTRA

T. C. Devore, M. McQuaid, and J. L. Gole

Three new electronic states of CrF and two electronic transitions tentatively assigned to a polyatomic " Cr_xF " (Cr_2F) emitter are observed in the chemiluminescent flame resulting from the reaction between entrained (He, CO) chromium vapor and molecular fluorine under multiple collision conditions. The CrF transitions are vibrationally analyzed and term symbols

assigned. Each of the new transitions correlates well with a previously observed transition in the "pseudo-isoelectronic" molecules MnO, CrH, or CrCl. This correlation provides a basis for determining the electronic configuration of the CrF states and a guideline for predicting unobserved electronic transitions in the "pseudo-isoelectronic" molecules.

CONTINUOUS CHEMICAL AMPLIFICATION OF SINGLE AND MULTI-MODE LASERS IN THE VISIBLE REGION

S. H. Cobb, J. R. Woodward, and J. L. Gole

The chemiluminescent spectrum for the $\text{Na}_3 + \text{Br} \rightarrow \text{Na}_2^* + \text{NaBr}$ reaction has been analyzed to determine that optical gain through stimulated emission characterizes certain distinct visible spectral regions. Broadband (0.5 cm^{-1}) laser gain measurements performed across the spectral region extending from 420 to 600 nm demonstrate gain in the regions of ~ 527 , ~ 492 , and ~ 460.5 nm, the maximum gain at ~ 527 nm being 1% of the input laser power. Single mode (0.007 cm^{-1}) laser gain measurements extending from 527.03 to 526.63 nm demonstrate that amplification involves four to seven rovibronic levels in this region. A maximum gain close to 3% is recorded in the single mode studies.

ELECTRIC FIELD ENHANCED LASER INDUCED PLASMA SPECTROSCOPY OF JET COOLED METAL CLUSTERS AND THEIR IONS

K. X. He, M. Diestler, M. Xu, E. Daykin and J. L. Gole

Electric Field Enhanced Laser Induced Plasma Spectroscopy is developed as a relatively simple and general first order approach to a mapping of electronic states and internal mode structure in small metal clusters and their ions. Neutral and ionic emission features are distinguished with a sorting procedure based on field enhancement. Results obtained for Cu_x ($x = 1-3$) and Cu_x^+ ($x \geq 1$) emission systems are used to exemplify the approach which has now also been applied to the aluminum, carbon, and iron systems. It is also suggested that this approach will be useful for a study of the corresponding metal hydrides in systems where the chemisorption of hydrogen is prevalent.

FORMATION OF THE LOW-LYING ELECTRONIC STATES OF CrO IN HIGHLY EXOTHERMIC REACTIVE OXIDATION - ASSESSMENT OF NEW STATES AND PARTIAL RESOLUTION OF PREVIOUS OBSERVATIONS

T. C. Devore and J. L. Gole

The highly exothermic reactions of chromium atoms with O_3 and N_2O have been studied over a pressure extended in a controlled manner from a single collision bimolecular reactive environment ($\text{Cr} + \text{XO} \rightarrow \text{CrO}^* + \text{X} (\text{O}_2, \text{N}_2)$) with $P_{\text{Total}} \leq 10^{-4}$ Torr to multiple collision conditions ($\text{Cr} + \text{XO} + \text{Ar} \rightarrow \text{CrO}^* + \text{X} + \text{Ar}$) with $P_{\text{Total}} (\text{Ar}) \approx 2000 \mu$. The multiple collision environment promotes rotational relaxation and allows the study of strong couplings and rapid energy transfer among CrO excited states. The combination of these studies provides further information on the CrO electronic state manifold. Emission is observed from two and possibly three different excited states of CrO including the well-known 600 nm system ($B^5\Pi - X^5\Pi$), a system at ~ 850 nm

($T_0 = 11800 \text{ cm}^{-1}$, $\Delta G_{1/2}' = 820 \text{ cm}^{-1}$) tentatively associated with an $A'^5\Delta - X^5\Pi$ transition, and a newly observed blue system in the range $\lambda\lambda 510\text{-}420 \text{ nm}$ ($E_{\text{onset}} \approx 22163$, $\Delta G \approx 575 \text{ cm}^{-1}$) which emanates either from a new electronic state or from higher vibrational levels of a strongly inflected $B^5\Pi$ state. Features associated with the $v' = 2, 3, 4$ and 5 levels of the $\text{CrO } B^5\Pi$ state display an apparent doubling into two components (bands) whose average frequency corresponds closely to that anticipated vibrational level structure for the $B^5\Pi$ state. This dual level structure is attributed to the interaction between two closely lying excited electronic states of CrO , one being $B^5\Pi$, the mixing being of such a magnitude that perturbations of the $B^5\Pi$ state extend across a large manifold of rotational levels leading to an apparent shift of this bundle of levels due to the interaction with a perturber state. The perturber state which borrows intensity from $B^5\Pi$ becomes the second component of the doublet structure.

**SPECTROSCOPY OF THE AlAr VAN DER WAALS COMPLEX:
ROTATIONALLY RESOLVED $B^2\Sigma^+ \leftarrow X^2\Pi_{1/2}$ ELECTRONIC TRANSITIONS**

Michael J. McQuaid, James L. Gole, Michael C. Heaven

Rotationally resolved spectra were recorded for six bands of the $\text{AlAr } B^2\Sigma^+ - X^2\Pi_{1/2}$ transition. Vibrational and rotational constants derived from these spectra were used to determine the upper and lower state potential energy curves. The accuracy of these potentials was assessed through calculations of the spectroscopic constants and Franck-Condon factors. Dissociation energies of $D_e = 440_{-8}^{+35} \text{ cm}^{-1}$ and $D_e = 180_{-10}^{+40} \text{ cm}^{-1}$ were obtained for the B and X states, respectively. The interaction between $X^2\Pi_{1/2}$ and the low-lying $A^2\Sigma^+$ state has been characterized by analysis of the ground state lambda doublet splitting.

Seminars and Invited Talks on NSF Sponsored Research

International Workshop on Ionized Cluster Beam Techniques, Tokyo and Kyoto, Japan (1986) - Invited Talk, "Formation and Oxidation of Intense Metal Cluster Beams and Flows".

20th Mid Atlantic ACS Meeting, Symposium on Clusters and Cluster Ions, Baltimore, Maryland (1986) - Invited Talk, "Preparation, Characterization, and Oxidation of Small Metal Clusters".

Optical Society: OSA Annual Meeting and APS/OSA International Laser Science Conference - Seattle (1987) - Invited Talk, "Preparation, Characterization, and Oxidation of Small Metal Clusters".

Department of Chemistry, University of Georgia (1987) "Formation and Oxidation of Metal Based CO and CO₂ Complexes".

Gordon Research Conference on Metal and Semiconductor Clusters (1987), "The Varied Dynamics of Metal Clusters and Their Oxidations".

Quarterly PICO Seminar - School of Physics, Georgia Tech (1987), "Chemically Driven Visible and Ultraviolet Lasers".

Gaseous Electronics Conference, Atlanta, Georgia (1987) - Invited Talk in Symposium on Molecular Clusters, "Preparation, Characterization, and Oxidation of Small Metal Clusters".

E. I. Dupont Nemours, Wilmington, Delaware (1987), "Metal Atom and Cluster Oxidations - What Are They Good For".

Third International Laser Science Conference, Atlantic City, New Jersey (1987), Invited Talk in Symposium on Molecular and Cluster Spectroscopy "Characterization of Cluster Formation in Metal Atom and Cluster Based Systems".

Third International Laser Science Conference, Atlantic City, New Jersey (1987), "A Chemical Process Showing Laser Gain in the Visible Region".

Southeast Regional A.C.S. Meeting, Orlando, Florida (1987) - Invited Talk, in Symposium on Optical and Dynamical Properties of Metal Clusters, "Preparation, Characterization, and Oxidation of Small Metal Clusters".

University of Iowa - Departments of Chemistry and Physics and Iowa Laser Facility (1987), Invited Talk, "Developing a Visible Chemical Laser".

Gordon Conference on High Temperature Chemistry (1988) - "The Varied Dynamics of Metal Clusters and Their Oxides".

196th ACS Meeting, Symposium on the Chemistry of Isolated Atoms and Clusters, Los Angeles (1988) - Invited Talk - "Metal Atoms and Cluster Based Complex Oxidation".

Fourth International Laser Science Conference, Atlanta, Georgia (1988) - "Formation, Characterization, and Oxidation of Metal Based CO and CO₂ Complexes".

Fourth International Laser Science Conference, Atlanta, Georgia (1988) - " A Chemical Process Producing a Continuous Laser Amplifier in the Visible Region".

40th Southeast Regional ACS Meeting, Atlanta, Georgia (1988) - Symposium on Metal Clusters - Invited Talk - "Metal Atom and Cluster Based Complex Oxidation".

Emory University Department of Physics, Atlanta, Georgia (1988) - Invited Talk - "Chemically Pumped Visible Lasers".

Furman University, Department of Chemistry, (1989) - Invited Talk - "Chemically Pumped Visible Lasers".

Short Wavelength Chemical Laser Workshop - Atlanta, Georgia (1989) - Invited Talk, "The SiO, GeO - Tl and Na₃ - X(Cl,Br,I) Laser Systems".

METAL CLUSTERS AND THEIR UNIQUE REACTION DYNAMICS

Because they represent bridging regions of molecular bonding, structure and reactivity, clusters of several atoms and metal clusters in particular are attracting the attention of physicists, chemical physicists, and chemists alike.¹ Not only can these species and their interactions be used to model the manner in which atoms and molecules come together to form bulk matter, but also they possess a unique and useful chemistry onto themselves. Sufficient evidence now exists to indicate that an increased knowledge of the behavior and reactivity of metal clusters heightens and elucidates our understanding of the fundamental mechanisms of catalysis, as bulk metals and metal clustered oxides influence and enhance the rate of many significant processes for the chemical production of widely used materials such as methanol. Further evidence is now accumulating to suggest that the concepts developed for the formation and characterization of metal clusters can be extended to the modification of the bulk metallic phase so as to create novel materials of low density combined with unusual hardness and unexpectedly low resistivity.¹ These materials, whose formation is controlled by kinetics or the rate at which chemical conversions occur rather than thermodynamics or the relative stability of reactant and product molecules, may prove useful in a variety of applications ranging from airplane construction to the development of improved electrical circuit components.

Although a number of elegant studies have emerged thusfar in this burgeoning field, these efforts have largely neglected the complex movements of groups of several metal atoms and the way in which this behavior influences the products formed in metal cluster reactions. The limited information which is available demonstrates that metal clusters undergo a very unique and in many instances totally unexpected reactive branching. Not only is the study of this reactive branching fundamental to the development of rules required to extrapolate from simple $A + BC$ reactions but also the study of the specific energy framework of the product metal clustered oxides and halides provides

detailed and fundamental information on molecular structure and bonding. The entire realm of cluster studies currently underway benefits from an analysis of this energy framework. In correlation with computer simulations of the forces which define molecular movement this data provides a benchmark for the generation of reliable descriptions which can be used to (1) model and improve the behavior of highly exothermic combustion processes such as those involving boron (see also following) which can provide more than twice the volumetric energy density of conventional and currently used hydrocarbon fuels, (2) model those local cooperative phenomena between metal atoms which influence reactivity and mobility and whose description can be very useful in the modeling at the interface of metal cluster oxide surfaces where, for example, catalytic behavior is most likely influenced, and (3) model the nature of metal cluster based interactions which influence the quality of a surface etch ($\text{Si}_n + \text{X}(\text{Cl}, \text{Cl}_2, \text{F}, \text{F}_2)$) as one fabricates microelectronic circuitry in this rapidly expanding industry or enhance understanding of the new class of high temperature superconductors (see also following). We wish to develop a description of the intimate environment associated with the metal cluster-oxygen or metal cluster-halogen interaction, determining (1) how clusters of metal atoms interact with the oxygen or halogen atom and (2) the dynamic behavior which these clustered atoms may exhibit as they move about the oxygen or halogen atom.

The major research impetus in our laboratory focuses on the experimental and theoretical treatment of metal clusters and the unique oxidation processes which they undergo. This research effort has included several breakthroughs.

We have demonstrated (see attached) the first chemically pumped continuous laser amplifier in the visible spectral region (green, blue, and purple light) based on the characterization of the sodium trimer (Na_3) + halogen atom ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) reactions. This effort, which stemmed from our laboratories study of sodium polymer - halogen atom reactions within the

general framework of exploring metal cluster oxidation, marks the end of a long (~ 20 year) and frustrating effort to push chemical lasers from the infrared into the visible region. Lasers which operate in the visible region are more easily focused, require simpler equipment, and can be more compact. They hold the further advantage of greater efficiency verses commercially available electrical lasers and provide the ability to work in space or remote locations where a portable energy source is necessary.

It is noteworthy that before this detailed study of the $\text{Na}_3\text{-X}$ reactive system was undertaken, no available theories or previous experiments predicted the unique reactive branching leading to the formation of this visible chemical laser amplifier. A full understanding of this system will surely lead to new insights into molecular bonding and reactivity.

In extending our study of metal cluster oxidation, we are completing the first phases of a group of studies in which we have observed and analyzed the optical signatures for the products of metal cluster oxidation, this work yielding important information on the kinetically controlled formation of the asymmetrical cluster oxides M_2O and M_xO ($x \geq 3$). It is significant that the metal cluster oxides and halides we generate represent the nonsymmetrical isomers, M_xO and M_xF (ex. $\text{Ag}_x\text{O}(\text{Ag}_2\text{O})$, $\text{Cu}_x\text{O}(\text{Cu}_x\text{O})$, $\text{B}_x\text{O}(\text{B}_2\text{O})$, Cr_xF , Al_xF) where a metal atom grouping is bound to the oxygen or halogen, rather than those compounds which might be synthesized through thermochemical means.

Not only do we study a new class of interactions, generating a new class of metal clustered compounds but the study of the asymmetrical isomers provides a closer parallel to the nature of reactions on a metallic surface and the catalytic action of such surfaces and complements the ongoing studies of neutral and ionic cluster reactivity now underway in a number of research groups. We establish structures and determine, through bond angle and vibrational frequency determinations, the manner in which metal clusters

interact with an oxygen or halogen atom when they are formed in a unique kinetically controlled environment. While these are difficult experiments, the bounty on success is high and can well be considered in terms of the individual systems chosen for investigation. It is appropriate that we detail the importance of these studies for a few systems involving the boron, copper, and silver cluster oxides.

Boron combustion can provide more than twice the volumetric energy density of conventional hydrocarbons. While the emphasis in boron combustion and fuel research has been largely on boron particle ignition, it is also recognized that as much as half of the potential energy content of boron rocket fuels can be released in gas phase oxidation processes which might be exemplified by the conversion of $\text{BO}(\text{g})$ to $\text{B}_2\text{O}_3(\text{g})$. With a focus on homogeneous combustion chemistry, elegant studies are now in progress to assess the specific details of the gas phase oxidation of $\text{BO}(\text{g})$ to $\text{B}_2\text{O}_3(\text{g})$. Here, the key BO oxidation step in dry atmospheres is thought to be the rate limiting oxidation $\text{BO}(\text{g}) + \text{O}_2(\text{g}) \rightarrow \text{BO}_2(\text{g}) + \text{O}(\text{g})$, followed by the subsequent reaction of BO_2 with additional BO molecules, the two step process producing $\text{B}_2\text{O}_3(\text{g})$. If $\text{BO}(\text{g})$ is a major constituent in dry atmospheres, it is likely that this molecule strongly influences the homogeneous combustion chemistry associated with boron oxidation. However, it is not certain that gaseous BO is the prime gas phase constituent liberated in the ignition of boron particulates, and several important gas phase compounds released as boron combusts might be neither gas phase $\text{BO}(\text{g})$ nor solid boron but rather intermediate species. It has been suggested that one of these species might be B_2O . If so, it is feasible that the process $\text{B}_2\text{O}(\text{g}) + \text{O}_2(\text{g})$ can compete with the two-step mechanism indicated above for $\text{B}_2\text{O}_3(\text{g})$ formation. It is up to the modern kineticist to assess this possibility, however, he can only be in a position to make this assessment with information on the energetics and energy level structure characterizing these boron clustered oxide molecules.

This is especially significant in the boron system where our studies of boron cluster oxidation have already demonstrated that the molecular electronic structure of the asymmetric and symmetric boron cluster oxides (BBO vs. BOB) and their energy level framework are quite different for even these "simplest" of cluster oxide isomers. This behavior is not readily discerned from simple molecular structure concepts. This data is now proving quite valuable to the boron kinetics group at the Naval Research Laboratory.

Our studies of the copper cluster oxides have now provided the impetus for the generation of models for the copper-oxygen interactions in these molecules. The models being generated for CuOCu and CuCuO are indicating that these molecules are bent but extremely floppy. These models are gauged by their fit of experimental vibrational frequencies generated in our initial studies. This modeling effort may well be relevant to the assessment of the role which the copper oxide lattice plays in high T_c superconductors. Here the movement of the copper and oxygen atoms as dictated by the Cu_xO potential function, especially the vibrational modes associated with the out-of-plane bending of these species, is thought to play an important role in the high T_c mechanism.

The chemistry of silver derives its technological importance from its use in photography and catalytic processes. The epoxidation of ethene is catalyzed by supported silver while the dehydrogenation of methanol is catalyzed by bulk silver both of which contribute extremely important industrial processes and products. In both systems, the silver catalyst must be in the form of a silver clustered oxide as are most metal catalysts. Studies which characterize these metal clustered oxides can be used to provide valuable insights into molecular structure, bonding, and atomic mobility in the Ag_xO constituents as an aid to their modeling in the bulk configuration. Valuable data for this modeling effort is gained from the study of Ag_2O and from the extension of these Ag_2O studies to the higher metal clustered oxides

Ag_xO ($x \geq 3$). In fact our current studies of the silver cluster oxides, which have been cited by the Silver Institute, appear to be contributing to our understanding of the behavior of these atomic groupings in the catalytic epoxidation of ethene. The results obtained thusfar have been communicated to the Los Alamos Scientific Laboratory theory group currently studying the ethene epoxidation process. Our studies of the Ag_xO system have now also sparked a collaborative extension to the corresponding Ag_xS sulfides. These compounds are believed to play an important role, through sulfide-halide interactions in film emulsions, thus they are of significant interest to the Eastman Kodak company.

Finally, we note that we have recently observed the optical signatures associated with the formation and oxidation of metal atom based CO and CO_2 solvation complexes. These complexes are representative of a virtually unstudied intermediate bonding region spanning the range, both as a function of the metal atom under study and experimental conditions, from weak binding Van der Waals interactions to the establishment of significant chemical bonds. The metal atom based CO complexes form a subset of the $\text{M}_x(\text{CO})_x$ ($1 \leq x \leq 3$) complexes whose properties also are expected to span this intermediate region. These compounds bear a greater significance as potential models for enhancing our understanding of one of the outstanding questions in heterogeneous catalysis. This question concerns the role of precursor states and the kinetics of transformation between these states and the chemisorption regime. With a focus on the metal surface carbonyl interaction, the $\text{M}_n(\text{CO})_x$ ($1 \leq n \leq 3$) clusters are pertinent to this question since they encompass a series of model compounds for which detailed microscopic information describing the intimate environment of the metal-carbonyl interaction can be extracted. It is precisely this information which can provide the productive tension between experiment and theory required for the development of systematically constructed and meaningful model systems representing the nature of ligand-

metal surface interactions.

A Science Service Publication
Volume 132, No. 17, October 24, 1987

This Week

definitive...
cine. One promise...
some aspect that all...
rhinoviruses have in common...
their structure or in how they...
humans, the only natural hosts of the cold viruses.

In the recent work, scientists at the University of Virginia in Charlottesville and Johns Hopkins University in Baltimore report that, regardless of the rhinovirus involved, proteins called kinins appear to be the primary cause of painful nasal congestion. Released from plasma proteins activated by enzymes, kinins in the blood cause expansion of blood vessels, which allows fluid to leak into surrounding tissue. This fluid accumulation and its pressure on nerve endings is responsible for characteristic cold symptoms. Although these effects were already known, the researchers were surprised by the close relationship between kinin levels and symptoms.

The study, to be published in the January JOURNAL OF INFECTIOUS DISEASES, shows that kinin levels increase as cold symptoms appear and then decrease as symptoms fade. "The striking thing was that the kinins reached a peak on day two or three [after infection], which coincided with the peak of symptoms," J. Owen Hendley of Virginia told SCIENCE NEWS.

Using nasal discharges from 40 volunteers infected with rhinoviruses, the researchers found that kinin levels increased 20- to 80-fold in the two-thirds who developed symptoms. What the scientists did not find, Hendley says, is a similar rise in the level of histamines, proteins released from tissue cells during allergic attacks that also dilate blood vessels. "Antihistamines have been used in common cold remedies for years," says Hendley. "But the evidence from studies in the past 10 years saying that they work [for colds] is marginal at best."

"Antikinins," however, may be more promising, says Hendley. Because there is a time gap between infection of nasal passages and the influx of kinins into tissues, he suspects that the viruses may be activating kinin production. Drugs to

260	Meningitis Vaccine Stirs Controversy
261	Cold cure, prevention: Nothing to sneeze at
261	Chemical power for visible-light lasers
262	Seamount serendipity in the South Pacific
262	Mood swings and creativity: New clues
263	Supernova X-rays: Too little too soon
263	A-bomb radiation doses reassessed

and foot-and-mouth disease viruses.

After making synthetic peptide structures that included these amino acid sequences, McCray and Werner injected them into rabbits. Antibodies produced

protection against infection, she says. Palmenberg and colleague Michael G. Rossmann discovered the surface cleft about two years ago while studying the structures of viruses. — D.D. Edwards

Chemical power for visible-light lasers

Energy generated directly by chemical reactions may soon power lasers capable of producing intense visible light. The recent development of the first visible-light chemical amplifiers marks the end of a two-decade search by scientists throughout the world for such systems. It also opens up the possibility of using lasers in remote locations such as space stations or satellites.

Conventional lasers rely on strong bursts of electricity to excite materials into emitting coherent light. Notoriously inefficient, such lasers require large quantities of electrical power to operate. Chemically powered lasers promise a more efficient way to generate intense light.

"It was a long road," says physicist James L. Gole of the Georgia Institute of Technology in Atlanta, who led the research. "What we have done so far is to demonstrate that these lasers amplify radiation." The next step, he says, is to build an oscillator consisting of a mirrored cavity that bounces light back and forth through the reaction zone.

"It's a significant development," says Terry A. Cool of Cornell University in Ithaca, N.Y., who years earlier had developed the first chemically powered infrared laser. Until Gole's persistence paid off, he says, scientists, despite trying many different approaches, had a long record of failure in their search for chemical reactions leading to molecules in excited states that would per-

mit light amplification.

In Gole's pulsed amplifier, thallium atoms pick up energy from collisions with excited molecules formed by a reaction between ozone and silicon or germanium. The collisions pump the thallium atoms up to an excited state. The atoms can then be stimulated to emit their radiation in a coordinated fashion to produce light amplification. The emitted light is green. When developed, says Gole, the system could turn out to be so powerful that it may be difficult to control.

Gole and his team have also developed a less powerful, continuous light amplifier based on the reaction between three-atom sodium clusters and halogen atoms. When a halogen such as chlorine reacts with a three-atom sodium cluster, the result is the formation of sodium chloride and an excited two-atom sodium cluster. The new cluster emits light, dropping to a lower energy level, and immediately reacts with any excess chlorine. Because this reaction is so rapid, the population of excited sodium clusters is always higher than that of low-energy clusters, allowing the laser to operate continuously.

Potential applications of chemically powered lasers depend not only on the possibility of achieving high powers but also on the fact that visible light requires simpler optics and is easier to focus than infrared radiation. Visible-light lasers are also likely to be quite compact.

— I. Peterson

TECHNOLOGY IN PERSPECTIVE

Optical chemical lasers take a quantum leap

Recent work at Georgia Institute of Technology has brought the chemically powered optical laser one step closer. Researchers have been looking for 20 years for visible laser amplifiers powered by chemical reaction. Now Georgia Tech researchers have discovered two laser amplifier systems—one continuous and one pulsed—which operate in the visual range. The work is an offshoot of research into chemical reactions being done for the National Science Foundation.

Chemical lasers could have a number of applications, particularly in space, the battlefield or any other environment where electricity is not readily available.

In laser action atoms or molecules in the laser medium are excited. When the number of excited atoms or molecules is greater than those in the lower energy levels, there is population inversion which gives the potential for the laser effect. With sufficient excited atoms or molecules there is the possibility that one atom or molecule falling back to a lower energy level and emitting a photon will stimulate another atom or molecule to do so also, giving amplification, a cascade of photons of the same frequency and in phases.

What the Georgia group has done is to produce this amplification in a chemical system. They have yet to oscillate this cascade of photons between two parallel mirrors to build up the sort of beam normally associated with conventional lasers.

In the continuous system the population inversion is produced by gas-phase molecules made up of three sodium atoms reacting with atoms of the halogens chlorine, bromine or iodine. The reaction gives a sodium halide molecule and an excited molecule of two sodium atoms. The excited molecule has the excess energy for a population inversion.

As the excited sodium molecules release their photons they react with excess halogen atoms. This reaction takes them out of the system and helps maintain the population inversion.

As explained by the leader of the research team James

ponent of the process is the fact that the excited sodium molecules emit light faster than they can react with the excess halogen atoms.

In the pulsed system there is rapid transfer of energy from a highly excited metastable metal oxide molecule to a thallium atom. The metal oxide molecule is formed by reacting silicon or germanium with ozone.

Thallium has an energy ground state which is split into two widely separated levels. When thallium is vaporised its atoms are in the lower of the

two ground states. The metal oxide molecules which are highly excited pass over their energy and pump the thallium atoms up to an excited state with respect to the upper level of the thallium ground state, creating the necessary population inversion.

These two initial systems produce green light but the team is working on similar chemical systems with the hope of light in the blue and violet sectors of the spectrum.

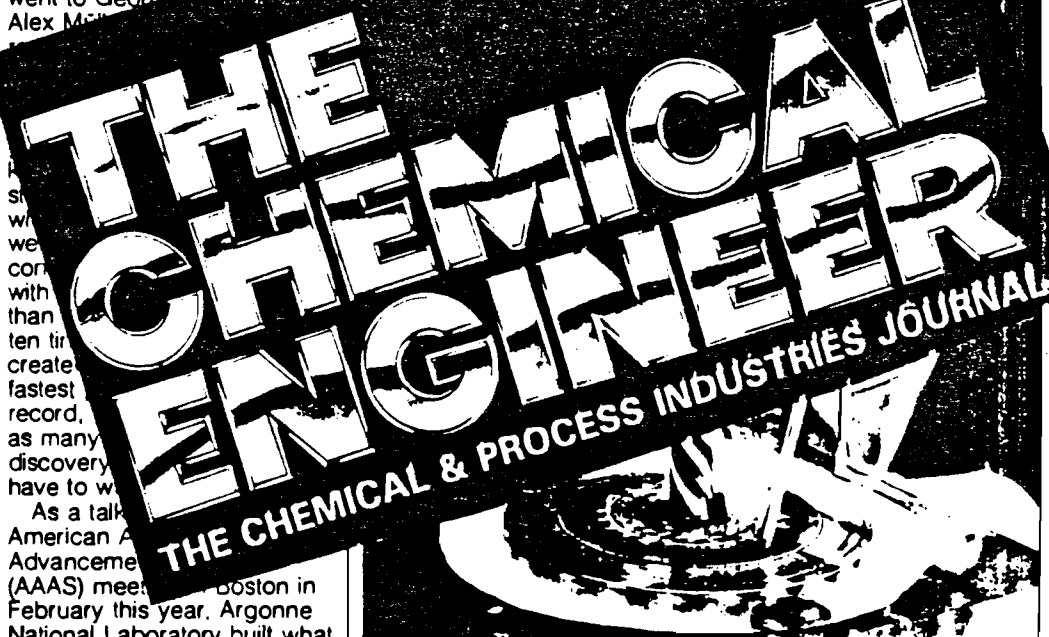
Dr Gole points out that these chemical lasers make more efficient use of energy

than conventional electrical lasers. "When you calculate how much energy you can channel into a system with a chemical reaction versus what you can put in with normal electrical means, you are much better off with the chemical approach," he says.

Chemical lasers operating in the lower energy infrared region of the spectrum already exist but they require large optical systems. Dr Gole points out that visible light lasers when developed will be easier to focus and will operate with simpler equipment.

Electric motor demonstrates superconductivity

As anyone who reads the scientific press must know superconductivity is the "hot topic" of the moment. Last year's Nobel Prize for physics went to Georgios Dimitropoulos and Alex Müller.



As a talk given at the American Association for the Advancement of Science (AAAS) meeting in Boston in February this year, Argonne National Laboratory built what it claims is the first electric motor based on the new high-temperature superconductors. The simple motor rotates at around 50 rpm. Although it produces little power it demonstrates some of the properties of superconductors rather elegantly.

Below the critical temperature superconductors show perfect diamagnetism. In a magnetic field a diamagnetic substance becomes magnetised in the opposite direction to the field and thus opposes it.

To exploit this effect the motor consists of a circular aluminium plate about 22cm

Richard McDaniel, a researcher in the ceramics section at Argonne, pours liquid nitrogen on the motor

edge are mounted 24 small electromagnets about 4 cm by 1.2 cm in size. The electromagnets are energised via a commutator on the plate and a carbon brush. This plate rotates above two discs made of yttrium-barium-copper oxide. These disks become superconducting at 94K.

As an electromagnet circles over a superconductor it is switched on, producing a magnetic field which induces the superconductor to produce an opposing mag-

netic field and pushing it.

Roger B Poeppel, manager of the ceramics section of Argonne's division of materials and components technology, claims, "We built it to show that simple, operating motors can be made with new superconducting ceramics. It is too small for practical use... but it demonstrates for the first time that these motors are possible."

After the AAAS in Boston the motor is going on show in the Museum of Science and

OE REPORTS

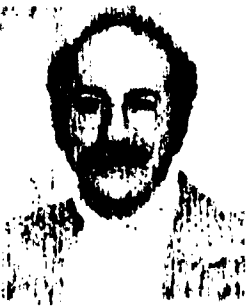
AVERAGE
MONTHLY
CIRCULATION:
50,000

♥ The International Newspaper of Optical and Optoelectronic Applied Science and Engineering

Medical imaging applications

An interview with Martin A. Afromowitz: Multispectral imaging of burn wounds

Martin A. Afromowitz received BS, MS, and PhD degrees in electrical engineering from Columbia University. He spent five years at Bell Labs in Murray Hill, working on III-V semiconductor LEDs and laser structures. In 1974 he joined the Center for Bioengineering at the University of Washington. He is now an associate professor of electrical engineering and an adjunct associate professor of bioengineering. His research interests include medical instrumentation, microfabrication, and optical fiber sensors. Afromowitz is coauthor of a paper to be presented in the Digital Medical Photography session of the Medical Imaging II: Image Formation, Detection, Processing, and Interpretation conference this month in Newport Beach, CA. He was interviewed recently by Robert Sol, SPIE Technical Consultant.



First of all, what do you mean by multispectral imaging of burn wounds?

Afromowitz: Multispectral imaging, to me, means taking a series of images simultaneously, or as simultaneously as possible, of a burn wound, in narrow wavelength ranges. We take images in the red, the green, and the near infrared.

Do you use a laser source?

Afromowitz: No, we use a white light source and a CCD camera with a filter wheel spinning in front of it to acquire the different wavelength images. The white light source is a standard photo flood

light source. On further inspection, they found out that that particular area of the burn turned out to be a third degree burn—a deep or full-thickness burn, which eventually needed to be grafted, whereas the other areas of the burn healed. So there was some suspicion that infrared photography can detect anomalous regions underneath the surface, and that there was some correlation of these anomalous regions with the burn-healing mechanism. Because the infrared image was also affected by the surface features of the burn, Anselmo and Zawacki also examined images in red and green light. Images were taken simultaneously through three different cameras, using filters in front of panchromatic film for the visible images and

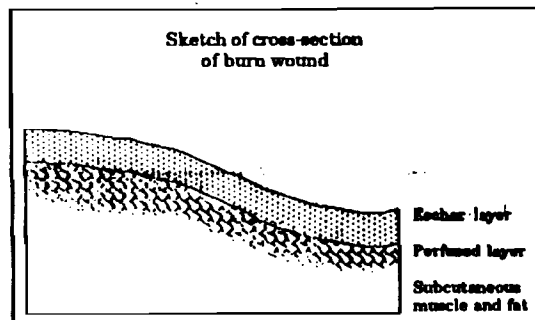


Figure 1. Sketch of cross-section of a burn wound.

infrared film and filters for the infrared images. The negatives of the three images of the burn—in the red, in the green, and in the near infrared—were digitized using a computer, and the ratios of intensities were calculated at each digitized pixel: red to infrared, green to infrared, and so on.

This issue's Focus

Medical Imaging

(see pages 4 and 5)

New visible light chemical lasers offer space applications

For 20 years, scientists have been searching for chemically powered visible lasers. Now physicists at the Georgia Institute of Technology have developed what are believed to be the first two chemical laser amplifiers operating in the visible spectral region.

The new laser amplifiers could have applications in space or in any environment where electricity to operate conventional lasers is not readily available, said James Gole, who heads the research group that

The group has succeeded in producing both continuous and pulsed visible laser amplifiers running solely on energy produced by chemical reaction..

developed the lasers. Conventional lasers require large electrical currents to generate the molecular changes that produce the laser effects.

The Gole group points out that these chemical lasers, developed in the Georgia Tech School of Physics, also make more

Fromowitz: Multispectral imaging, to me, means taking a series of images simultaneously, or as simultaneously as possible, of a burn wound, in narrow wavelength ranges. We take images in the red, the green, and the near infrared.

Q: Do you use a laser source?

Fromowitz: No, we use a white light source and a CCD camera with a filter wheel spinning in front of it to acquire the different wavelength images. The white light source is a standard photo flood quartz halogen lamp.

Q: How did interest in this procedure arise?

Fromowitz: Back in the mid-70s, I became aware of some work that

The ratios of red to infrared, red to green, green to infrared seemed to correlate with the depth of the burn. It was the first indication that a colorimetric analysis of a burn would be useful.

was published in the Proceedings of the SPIE by two researchers in California—Victor Anselmo, of the Jet Propulsion Laboratory, and Bruce Zawacki, a burn surgeon in Los Angeles. Their first article showed that, by using infrared photography, they were able to detect dark amorphous regions on a burn wound which had no surface correlate. They saw a darker region on an infrared image of a burn on a child's back; the surface features were not especially different at that point. They assumed they were seeing something underneath the surface, because infrared light can transmit through tissue farther

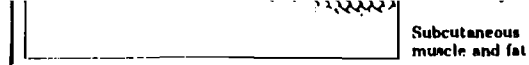


Figure 1. Sketch of cross-section of a burn wound.

infrared film and filters for the infrared images. The negatives of the three images of the burn—in the red, in the green, and in the near infrared—were digitized using a computer, and the ratios of intensities were calculated at each digitized pixel: red to infrared, green to infrared, and red to green. They were able to show, on a very limited number of patients, that these ratios seemed to correlate with the depth of the burn. And that was very exciting. It was the first indication that a colorimetric analysis of a burn would be useful at all.

The digitization of the negatives took several weeks to accomplish and was a fairly expensive process in those days. Because of the time lag in getting information back from photographic processing and computer densitometry, the patient had to be dealt with in the clinic before any information came back from this method; so it wasn't a useful clinical tool.

Q: So what was needed was a real-time measurement tool?

Fromowitz: Yes. But I started looking into the development of a bedside, real-time instrument that would take the same measurements, just to see what kind of information such a method would give. And since Anselmo and Zawacki's work was terminated by NASA at the time there wasn't any more information forthcoming from that source. So I built a small instrument, basically a spot meter, with a hand-held probe that illuminated a small selected

(continued on page 4)

duced by chemical reaction..

developed the lasers. Conventional lasers require large electrical currents to generate the molecular changes that produce the laser effects.

The Gole group points out that these chemical lasers, developed in the Georgia Tech School of Physics, also make more efficient use of energy than electrical lasers.

"When you calculate how much energy you can channel into a system with a chemical reaction versus what you have to put in with normal electrical means, you are much better off with the chemical approach," Gole said. The Georgia Tech group has succeeded in producing both continuous and pulsed visible laser amplifiers running solely on the energy produced by chemical reaction.

Although the researchers had been searching for a visible chemical laser on and off for a decade, the discovery of the continuous laser amplifier came as an offshoot of research on chemical reactions being done for the National Science Foundation.

"We recognized that we had observed the earmark of stimulated emission when

(continued on page 2)

Society of Photo-Optical Instrumentation Engineers
P.O. Box 10, Bellingham, WA 98227-0010 USA

Non Profit Org
U.S. Postage Paid
Society of
Photo-Optical
Instrumentation
Engineers

TABLE OF CONTENTS

Technology Transfer.....3	Symposium Announcements.....9
Optics Entrepreneur Interview.....3	Optomechanical Update.....11
Optical Storage of Medical Images.5	Optonet: Industry Briefs.....14

65149
Dr. Donald C. O'Shea
Georgia Institute of Technology
Department of Physics
Atlanta, GA 30332

oer2

dynamic laser or medical imaging.

On another topic, we note with pride the publication of the 50th issue of *OE Reports*. Just over four years ago, SPIE published the first issue, and it's been a period of growth for the paper and for everyone involved. We are grateful for your readership and support, and look forward to continued progress over the next 50 issues!

Robert E. Fischer, Editor of OE Reports, is manager of U.S. operations for Ernst Leitz Canada Ltd. He is a past president of SPIE and currently serves as chairman of SPIE's Long Range Planning Committee, and as a member of the Education Committee.

Visible light chemical lasers

(continued from page 1)

"we studied these chemical reactions," Gole explained. "We probably would not have recognized that very easily if we had not been familiar with the chemical laser work."

Chemical lasers operating in the lower energy infrared spectral region already exist, but Gole said visible lasers, once developed to their full capacity, will be easier to focus and operable with simpler equipment.

The group, which also includes Stephen H. Cobb and J. Robert Woodward, is now attempting to convert the amplifier systems to laser oscillators. The two initially discovered Georgia Tech lasers produce green light, but Gole reports that additional research underway on similar chemical systems indicates the promise of blue and violet light.

The operation of any laser depends on creating a substantial population of highly excited molecules. When the number of highly excited molecules exceeds the number of molecules in lower energy levels, a population inversion exists which creates the potential for the lasing effect.

The continuous laser amplifier creates a population inversion by reacting molecules composed of three sodium atoms (Na_3) with atoms of halogen (chlorine, bromine or iodine). This reaction forms sodium halides (NaX), which possess the excess energy required to place them in the higher energy levels needed for a population inversion.

As the excited sodium molecules release light, they relax to their lower energy ground state, where they immediately react with excess halogen atoms. This reaction takes these molecules out of the system, maintaining the population inversion and allowing the laser to operate continuously.

An important aspect of this process, Gole explains, is that the excited sodium (Na_3) molecules emit light at a rate faster than they

can react with the excess halogen atoms.

The pulsed amplifier relies on the rapid transfer of energy from a highly excited metastable metal monoxide molecule to a thallium atom. The excited metal oxide molecule is formed through the reaction of silicon or germanium with ozone. Thallium was chosen because its ground state is split into two widely separated levels.

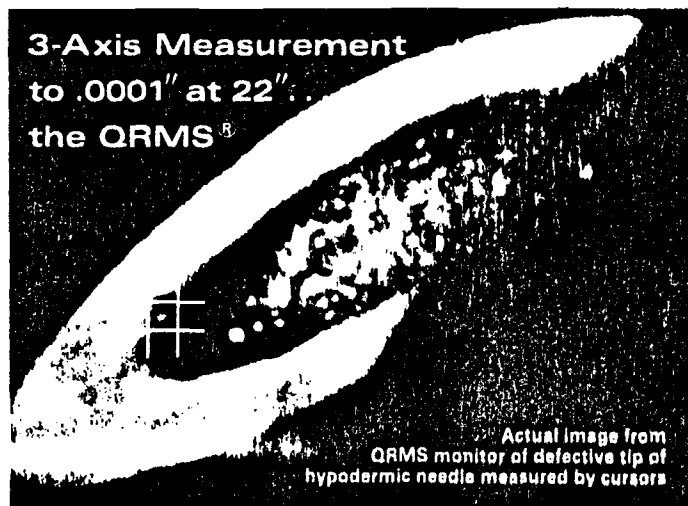
Upon vaporization, the thallium atoms are in the lower of the two energy levels. When they receive energy from the highly excited metal oxide molecules, the thallium

atoms are pumped to an excited state with respect to the upper level of the thallium atom ground state, creating the necessary population inversion.

The search for chemically driven visible lasers has occupied researchers for two decades, Gole noted.

"The number of approaches that have been taken in attempts to make this laser would probably take about seven pages to list," he added. "There have been many possibilities, but until now, they all had some flaw."

3-Axis Measurement to .0001" at 22" the QRMS®



Actual image from QRMS monitor of defective tip of hypodermic needle measured by cursors

Questar announces its Remote Measurement system—the QRMS—an AT-based, keyboard-controlled and menu-driven gauging, alignment and imaging system. Non-contact digital imaging calculates linear and angular measurement in 3 axes with on-line monitoring in a high-speed production environment without disturbing the process. Calibrates without reference. Full image and archival capabilities. Can include numeric and status

real processing of data. Portable. A powerful tool for research and production. You no longer need to stop the process, remove the part, inspect the part, replace the part. You simply **measure it...control it...document it**.

QUESTAR

Questar Corp., Dept. C-17, New Hope, PA 18938
(610) 765-1100 • Telex 506 3377

Correction

Dr. Robert Alfano, featured in an article in last month's *OE Reports*, was honored as Distinguished Professor of Science and Engineering, not physics as reported, at City College of the City University of New York.

OE Reports

OE Reports (ISSN 0764-5931) is published monthly by SPIE—The International Society for Optical Engineering. *OE Reports* is distributed without charge to U.S.-based optical, electro-optical, and optoelectronic applied scientists, engineers, technicians, R&D managers, original equipment manufacturers, and marketing professionals in industrial, governmental, and educational organizations, and to SPIE members worldwide. Average circulation: 50,000.

Editor: Robert E. Fischer
Managing Editor: Rich Donnelly
Advertising Manager: Diane Robinson
Advertising Sales: Kirk Knutsen
Contributors: John Powers, Frederick Su
European Correspondent: Roger P. Mann
Graphic: Kelly Anderson, Kelli McNamara, Matt Treat
Compositors: Christal Ballhazoor, Carrie Binschley, Teresa Larson
Technical Consultants: Rick Lemberg, Roy Potter

Address all submissions to Editor, *OE Reports*, SPIE, P.O. Box 10, Bellingham, WA 98227-0010 USA. Telephone: 206/676-3290. Telex: 467053. Reprinted articles in *OE Reports* reflect the author's opinion; inclusion in this publication does not necessarily constitute endorsement by the editors or by SPIE. *OE Reports* is a registered trademark of the Society of Photo Optical Instrumentation Engineers. Advertising is accepted at the discretion of the publisher.

SPIE—The International Society for Optical Engineering (Society of Photo Optical Instrumentation Engineers) is a non-profit educational society dedicated to advancing engineering and scientific applications of optical, electro-optical, and optoelectronic instrumentation, systems, and technology. It monitors and scientists, engineers, and users not only in the production to practice of these technologies. SPIE provides the means for continuing study and development, new developments and applications to the scientific, engineering, and commercial communities through its publications and symposia.

Copyright © 1988 Society of Photo Optical Instrumentation Engineers. All rights reserved.

SPIE—The International Society for Optical Engineering, P.O. Box 10, Bellingham, WA 98227-0010 USA. Telephone: 206/676-3290. Telex: 467053. European Office: Koldener Strasse 31, D-5300 Bonn 2, Federal Republic of Germany. Telephone: 02/5716 15 06. Telex: 112 254 110. Telex: 225 37 11. Inhabitat FAX: 02/5716 41 05.

LASERS

High efficiency keys interest in visible chemical lasers

PHYSICISTS AT Georgia Institute of Technology, Atlanta, have developed two chemical laser amplifiers that produce visible laser light. The work marks the first time that researchers have been able to generate visible laser light by a chemical method.

Chemical lasers operating in the lower-energy infrared spectral region already exist, but research has been geared toward chemical lasers operating in the visible spectral region because they promise to be easier to focus and operate. Primary uses for such systems are space and military applications, but the benefits that the laser could provide may translate into more uses than this, said Dr. James Gole, who directed the research.

Robert Woodward who, along with Stephen Cobb, also worked on the project, said, "The importance of a chemical process for a visible laser is that it is going to be extremely efficient.

"All of the commercial lasers now use some sort of large electrical supply to power them and they are not efficient—less than 1% normally. But in a chemical process most of your energy is going to be channeled into producing the light that you want to see," he told *R&D*.

The Georgia Tech group succeeded in producing continuous and pulsed chemical-laser amplifiers. Their discovery actually was an offshoot of research into chemical reactions they were doing for the National Science Foundation.

"We were initially studying these [compounds] from a chemical reactions standpoint, and noticed that situations

were arising where we expected to see laser emissions, and then we pursued it ourselves," Woodward said.

Creating a laser amplifier requires achieving a population inversion—a state where highly excited molecules outnumber the molecules in lower-energy states. For the continuous laser amplifier, a population inversion was created by reacting molecules composed of three sodium atoms (Na_3) with atoms of a halogen (chlorine, bromine, or iodine).

This reaction forms sodium halide molecules and molecules consisting of two sodium atoms (Na_2), which possess the excess energy required to put them in the higher-energy levels needed for a population inversion. As the excited sodium molecules release light, they relax to their low-energy ground state where they immediately react with excess halogen atoms.

This reaction takes these molecules out of the system, maintaining the population inversion and providing continuous laser operation.

The pulsed laser amplifier relies on the rapid transfer of energy from a highly excited metastable metal-monoxide molecule to a thallium atom. The excited metal-oxide molecule is formed through the reaction of silicon or germanium with ozone.

Upon vaporization, the thallium atoms are in the lower of their two energy levels. When they receive energy from the highly excited metal-oxide molecules, the thallium atoms are pumped to an excited state with respect to the upper level



Georgia Tech researchers Dr. James Gole, Robert Woodward, and Stephen Cobb (l to r) developed a chemical laser amplifier that produces visible (green) light.

of the thallium atom ground state, creating the necessary population inversion.

The researchers now are developing oscillator systems for the observed chemical reactions to make the light coherent. They also are experimenting with other possible chemical amplifiers, Woodward said.

"We are working on other chemical reactions involving the same idea, the same theory, to make light in different regions. Right now we can make green laser light, but by selecting a slightly different compound and doing analogous experiments, we might be able to produce blue and violet lights, which are more energetic than green light," Woodward explained.

"This will allow more applications or a wider range of wavelengths to choose from" for the chemical laser, he added.

—Skip Derra □

COMPUTERS

Advances in electronics spur interest in neurocomputers

THE EMERGENCE of a new computer concept that may have a dramatic effect on information processing techniques of the future was evident at the First Intl. Conference on Neural Networks. As indicated by the papers presented at the symposium, an increasing amount of R&D is being devoted to computer systems that attempt to mimic neural networks of the human brain.

The idea of doing this is not new, with pioneering work having been performed more than 30 years ago. However, the state of the art being what it was at that time, more progress toward practical computing techniques could be made by following other avenues, and neurocomputing essentially remained dormant until around 1982.

It was at this time that researchers,

such as Dr. John Hopfield of Caltech and AT&T Bell Labs, and Dr. Stephen Grossburg of Boston Univ. (both of whom presented papers at the conference), helped spawn new interest among scientists in physics and optics which resulted in an upsurge of work in the field.

A contributing factor was the great increase in the past 10 years in understanding the brain's way of working. As one conference speaker, Dr. Carver Mead of Caltech, recalled, the picture that biologists had of the brain 20 years ago "was much more simplistic and much less analog in nature. At the time, neurobiologists were preoccupied with nerve impulses and the way they were generated in neurons.

"Now they are looking more deeply at the principles on which neural compu-

tation is based, and there are some surprises here. Nerve impulses, which are quasi-digital, play a surprisingly small role in the actual computation process," Mead said.

"Most of the computation is analog and it's done at the very tips of the dendritic tree of the neuron. Throughout the brain there is a distributed feedback from these dendritic tips to the nerves that are driving them."

Such findings, he stressed, caused computer experts to look into synthesizing systems with some neural-type properties. The timing proved right, not only because of new insights into brain functions, but also because of advances in digital technology, such as the ability to make 6-in. chips with 1×10^9 transistors.

In typical digital use, many of the

Pamela Knight
News Editor

(201) 568-4744

Mail to: P.O. Box 1304, Fort Lee, NJ 07024
Offices at: 32 North Dean St., Englewood, NJ 07631

INSIDE R&D®

THE WEEKLY REPORT ON TECHNICAL INNOVATION

ISSN 0300 — 757X

December 23, 1987

New Sensor Measures Sub-picosec Electrical Pulses: Noninvasive probe for testing and designing integrated circuits measures pulses 100 times faster than conventional electronic sensors. AT&T researcher developed the electrooptic technique to work with any kind of circuit material, from Si and GaAs to ceramics and hybrids. Sensor resolves signals of less than 0.3 picosec. No specialized circuit designs are needed to accommodate testing, as with commonly-used sampling oscilloscope technique.

Key element is electrooptic crystal of lithium tantalate with a tip only 40 μ dia. Crystal is mounted below a high-resolution microscope on a quartz support rod that positions it near test point on the IC. Local electric field corresponding to voltage variations in conducting lines of the circuit affects crystal's optical properties. Subpicosec laser directed through the crystal translates optical changes into voltage data. Sensor lets chip designers zero in on electrical properties of features only microns wide to test and refine circuits.

Details: Janis Valdmanis, AT&T Bell Laboratories, 600 Mountain View, Murray Hill, NJ 07974. Phone: To reach Dr. Valdmanis, call Kevin Compton, 201-564-4097.

Heterojunction Transistor Promises to Double Speed: New type of bipolar transistor developed by IBM, silicon-germanium base heterojunction transistor, has potential to significantly extend performance limits of silicon bipolar technology. Bipolar transistors use both positive and negative charge carriers and are intrinsically faster than other transistor types, such as the field-effect transistor. They are used in supercomputers and large main-frame computers. With new design speed will be increased further.

SiGe alloy forms the middle (base) layer through which charge carriers travel. Alloy gives new transistor better electronic control compared to conventional homojunction (Si only) base transistors. Advantages include lower base resistance, higher emitter injection efficiency, and ability to operate at very low temperatures. New circuits work at 77°K (liquid nitrogen temperature).

Researchers use molecular beam epitaxy (MBE) to build the heterojunction and align crystalline structure. Technique is being used to grow SiGe crystals less than 1000 Å thick.

Details: S. S. Iyer or G. L. Patton, Thomas J. Watson Research Center, P.O. Box 218, Yorktown Heights, NY 10598. Phone: To reach Iyer or Patton, call Tom Murphy, 914-945-3036.

Visible Chemical Lasers: Georgia Tech researchers have developed chemical laser amplifiers that operate solely on energy from chemical reaction. Previous designs for chemical lasers operated only in the infrared spectrum. New lasers produce green light, so are easier to focus and can be operated using simpler equipment. Other advantages are greater efficiency, compared with electrical lasers, and ability to work in space or other remote locations where portable energy source is a plus.

Researchers made two types of chemical lasers -- continuous and pulsed. Continuous laser creates population inversion by reacting sodium trimers with halogen atoms (chlorine, bromine, or iodine). Sodium dimers and sodium halides are formed, releasing light energy. Pulsed system relies on rapid transfer of energy from an excited metastable metal monoxide molecule to a thallium atom. Energized thallium creates the population inversion.

Current goals are to expand capabilities to include emission of blue and violet light, and convert the amplifiers to laser oscillators.

Details: James Gole, School of Physics, Georgia Institute of Technology, Atlanta, GA 30332. Phone: 404-894-3444.

NEWS

with full electron shells are neodymium-like ions, with 60 electrons, and there are no stable elements with atomic numbers high enough to produce short wavelengths. In essence, you run out of electrons to remove.

Hagelstein, who left Livermore in early 1987 to join the faculty at the Massachusetts Institute of Technology, is more interested in scaling to longer wavelengths. The reason is that comparatively modest power levels should suffice to remove enough electrons to produce gain. He says nickel-like molybdenum could emit near 20 nm; that would require stripping only 14 electrons from the molybdenum atoms. He thinks a \$250,000 benchtop system might be able to do the job, putting extreme ultraviolet sources within the reach of small laboratories. He is waiting to get equipment he needs to begin experiments.

Personal experience makes Hagelstein sympathetic to the needs of "little science." It took a couple of years to

get time on Nova for the nickel-like laser experiments. He believes more smaller-scale short-wavelength sources would encourage more research in the field.

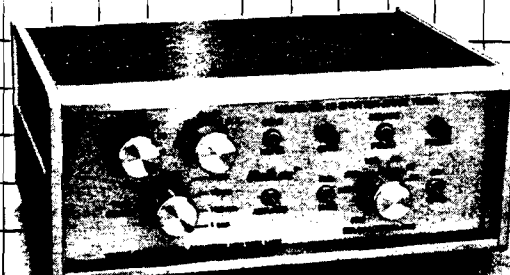
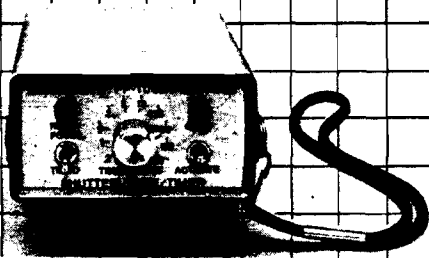
—Jeff Hecht

Chemical Laser Amplifies In Visible

After two decades, the search for visible-wavelength chemical lasers is starting to pay off. James L. Gole, Stephen H. Cobb and J. Robert Woodward of the Georgia Institute of Technology have measured laser gain at visible wavelengths in two chemically-driven systems. Although they have yet to demonstrate oscillation—which most observers consider a prerequisite for using the word "laser"—their experiments appear to mark the

end of a long and frustrating effort to push chemical lasers from the infrared into the visible region.

Visible chemical lasers have long been near the top of the military's laser wish list because of the prospects of greater portability and more efficient operation than electrically powered lasers. The infrared wavelengths of present-day chemical lasers have limited their practical applications. Large optics are needed to focus the beams tightly, and most target materials have low absorption at infrared wavelengths. Nonetheless, years of sponsoring futile projects led military agencies to write off the quest, although the Strategic Defense Initiative included visible chemical lasers on its long list of possible "Innovative Science and Technology" research. Ironically, the Georgia Tech results were the outgrowth of basic research into reactions of sodium trimers with halogens, sponsored by the National Science Foundation, and was not the

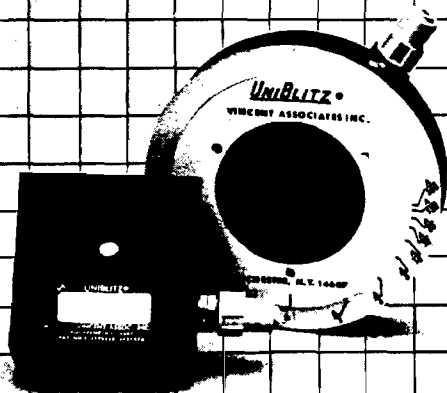


OVER AND OVER AND OVER...

Over 10 million exposures without replacement.

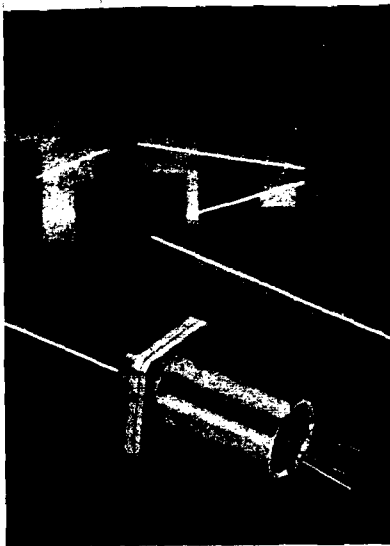
Our shutters work faster and longer—over and over and over. In fact, with our special "S" stop modification on models 214 and 225, you'll benefit from over 10 million exposures without replacement.

For precise, repeatable exposure control in image analysis, photolithography, optical research, spectral analysis and other applications, specify shutters and drive systems from Vincent. We work on and on for the best names in the business. With over 16 years of experience, we can help you with your applications problems, and provide fast response. Call today and see for yourself.



VINCENT ASSOCIATES
1255 University Avenue
Rochester, New York 14607

(800) 822-6972 in N.Y. State, call (716) 473-9232



Mitsubishi Transforms LAN Design.

Mitsubishi unleashes the tools that are completely transforming traditional approaches to LAN design. In system cost savings alone, they begin a new era for high performance LANs.

Mitsubishi's 780nm laser diode modules (the FU-05LD-N and FU-06LD) can be used with lower cost, short wavelength Si detectors, in short to medium haul applications. They're connectorized for fast, easy installation. And, with an MTBF of over 8 million hours (at 25°C), they'll still be working generations from now.

Two new Mitsubishi tools, ready in volume to reduce system costs and assure high reliability.

- Short wavelength laser diodes (780nm)
- Data rate up to 600Mb/s
- High power (1mW)—allows multi-drop architecture
- Connectorized (FU-05LD-N: FC-type; FU-06LD: SMA-type)



Mitsubishi Electronics America, Inc., Semiconductor Division
1050 East Arques Avenue, Sunnyvale, CA 94086.
(408) 730-5900. Ext. #2314

NEWS

result of a systematic effort to develop chemical lasers.

Both systems operate on green transitions in metal vapors. The first system demonstrated relies on the reaction of a halogen atom with a sodium trimer, Na_3 . Chlorine, bromine, or iodine atoms react with the Na_3 molecules to form a sodium halide and an excited sodium dimer, Na_2 . The highly exothermic reaction between the sodium molecules and halogen atoms in crossed beams produced bright fluorescence from Na_2 with sharp emission regions. By passing a dye laser beam through the reaction zone, Gole, Cobb, and Woodward detected a population inversion. They measured maximum laser gain at 527 nanometers of up to 1 percent of the probe beam power, corresponding to a gain coefficient of 0.002 per centimeter. They also observed superradiant emission from 524 to 530 nm.

The Georgia Tech group vaporizes metallic sodium in an oven operating at 950 to 1100 K, then passes the vapor through a supersonic nozzle into a reaction chamber at pressures of 10^{-5} to 10^{-6} torr. The rate of trimer production is low; at best, the ratio of sodium atoms, dimers, and trimers is about 1:1:0.03. However, Gole reports the reaction had an "extremely efficient inversion process," and that laser amplification was observed for 20 to 40 minutes. Reaction of halogen atoms with sodium dimers effectively depopulates the lower laser level, maintaining the population inversion.

In their second system, chemically produced silicon or germanium monoxide transfers energy to atomic thallium vapor. Reaction of ozone with atomic silicon or germanium atoms forms excited SiO or GeO molecules. These excited molecules are mixed with thallium atoms evaporated from an oven, and transfer energy from the excited SiO and GeO molecules to thallium's resonant $7^2_{1/2}$ level. This produces a population inversion, with the lower level being the upper of two levels of thallium's split ground state.

The thallium system produces bright green pulses at 535 nm. Because no fast mechanism removes atoms from the lower laser level, stimulated emission reduces the population inversion.

Like the nitrogen laser, the thallium emission is self-terminating.

Gole's group is exploring ways to extend their chemical pumping schemes to different systems and wavelengths. They believe the sodium-dimer system might work at shorter wavelengths, with the most attractive regions near 412.5, 395, 365, and 350 nm. They also are investigating prospects of extending the energy-transfer scheme to produce 451- and 417-nm emission from gallium and indium atoms.

Other efforts include trying to move beyond their present laser amplification experiments to demonstrate laser oscillators, and to scale to higher powers. "I would be very loathe to say there would be no problems," Gole said. However, he is optimistic that oscillation is possible as long as design and engineering "can be carried off as we think it can."

The Georgia group has yet to wrap up contracts for follow-up research, but Gole says they are exploring possibilities. One plan is a research partnership with the Tetra Corp. of Albuquerque to seek research contracts to raise power levels by scaling production of metastable SiO and GeO states.

— Jeff Hecht

ENTERTAINMENT & DISPLAY

Holographic Museum Opens In Los Angeles

Los Angeles now has its first holographic museum—the third in the nation. The new museum is called Holographic Visions and was officially opened on December 9, 1987 by Mayor Thomas Bradley. Mayor Bradley presented a plaque to the museum's founders, Chris Outwater and Jerry Preston, and proclaimed it Holographic Vision Day in Los Angeles. During the ceremony, Mayor Bradley also unveiled a large animated rainbow hologram of himself that was shot just the week before the opening.

Holographic Visions has a prime location in downtown Los Angeles, right next to the Museum of Contemporary