Final Technical Report

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

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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 Na₃ + X (X = Cl, Br, I) reactions. We have developed a source configuration which has allowed the first analysis of middle transition metal cluster (Ni₃) 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 M₂O and MₓO (x ≥ 3). It is significant that the metal cluster oxides we generate represent the nonsymmetrical isomers, MₓO, 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 CO₂ 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 Li₂, Na₂, LiH, and NaH and the alkali cation affinities of N₂, CO, and H₂. These studies represent the lead to the future study of the Li₂H⁺ and Na₂H⁺ 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


"Stability and Oxidation of Metal Based CO and CO2 Complexes", with M. J. McQuaid, 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.

Abstracts of Published Journal Articles

**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 = 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 ($K_{Knudsen} \times 1$), 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 non-effusive 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 ($Cu_x + O_3$), silver ($Ag_x + O_3$), boron ($B_x + NO_2, N_2O$), 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, $M_nO_y$. 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 Na_3-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 Å, corresponding to a gain coefficient of $2 \times 10^{-3} \text{ cm}^{-1}$. 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 C₂ᵥ (bent) for MH₂⁺ and Cᵥ (linear) for MCO⁺, MOC⁺, and MN₂⁺. The Li⁺ affinities (ΔH at 300 K) for H₂, CO (at 0), 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 0), 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 Δν = 0, Δν = 40 cm⁻¹ sequence grouping and a weaker Δν = +1 sequence (Δν = 40 cm⁻¹), 440 cm⁻¹ to higher energy. A second sequence with Δν-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 A10 B²Σ⁺ state or, in the case of CO₂, a polyatomic complex are compared to that A10 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-0O2 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 Eₚbinding(Ti(CO)ₓ) =1.75 eV and Eₚbinding(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 MnₓO 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
The lowest-lying MnO* \( A^7\Sigma^+ \) excited electronic state (Mn+O\(_3\)+Ar(He) \( \rightarrow \) MnO* \( A^7\Sigma^+ \) + O\(_2\) + Ar(He)) produces a strong chemiluminescent signal corresponding to the MnO \( A^7\Sigma^+ \) - \( X^5\Sigma^+ \) 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 MnO 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

\[
v_{v_1', v_1', v_3'} = 12512 + 600v_{11'} - 534v_{11'} + 360v_{33'} - 306v_{33'}
\]

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 an 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 \((\text{Mn-Mn})^{-1-0}\).
The B-X transition which originates at 506 nm is well fit by the expression

\[ n^2 = 19766 - 442v_1 - 165v_2 - 256v_3 + 6v_1^2 + 6(v_1^2)(v_2^2) \]

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 \( \text{B}_x^2 \pi \) symmetry. 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 \( MO_2(M=Na...Cs) \) 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 Na3 + Br → Na2* + 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 Cuₙ⁺ (x = 1-3) and Cuₙ⁺⁺ (x ≥ 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 O₂ and N₂O have been studied over a pressure extended in a controlled manner from a single collision bimolecular reactive environment (Cr + XO → CrO* + X (O₂,N₂)) with PTotal ≤ 10⁻⁴ Torr to multiple collision conditions (Cr + XO + Ar → CrO* + X + Ar) with PTotal (Ar) ≤ 2000 Torr. 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 (B³π - X³π), a system at ~850 nm
(v = 11800 cm⁻¹, ΔG'₁/₂ = 820 cm⁻¹) tentatively associated with an A'⁵Δ - X⁵Π transition, and a newly observed blue system in the range λλ 510-420 nm (E_onset = 22163, ΔG' = 575 cm⁻¹) which emanates either from a new electronic state or from higher vibrational levels of a strongly inflected B⁵π state. Features associated with the v' = 2,3,4 and 5 levels of the CrO B⁵π state display an apparent doubling into two components (bands) whose average frequency corresponds closely to that anticipated vibrational level structure for the B⁵π state. This dual level structure is attributed to the interaction between two closely lying excited electronic states of CrO, one being B⁵π, the mixing being of such a magnitude that perturbations of the B⁵π 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 B⁵π becomes the second component of the doublet structure.

SPECTROSCOPY OF THE AlAr VAN DER WAALS COMPLEX:
ROTATIONALLY RESOLVED B²Σ⁺ - X²Π₁/₂ ELECTRONIC TRANSITIONS

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

Rotationally resolved spectra were recorded for six bands of the AlAr B²Σ⁺-X²Π₁/₂ 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 cm⁻¹ and D_e = 180_10 ± 40 cm⁻¹ were obtained for the B and X states, respectively. The interaction between X²Π₁/₂ and the low-lying A²Σ⁺ 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".


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".


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".


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

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".

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 \( \text{Si}_n + \text{X(Cl,Cl}_2,F,F_2 \) 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 \( \text{Na}_3 \) + halogen atom \( \text{X = Cl,Br,I} \) 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 Na$_3$-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$_2$O and M$_x$O ($x \geq 3$). It is significant that the metal cluster oxides and halides we generate represent the nonsymmetrical isomers, M$_x$O and M$_x$F (ex. Ag$_{x}$O(Ag$_2$O), Cu$_x$O(Cu$_x$O), B$_x$O(B$_2$O), Cr$_x$F, Al$_x$F) 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 BO(g) to \(\text{B}_2\text{O}_3\)(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 BO(g) to \(\text{B}_2\text{O}_3\)(g). Here, the key BO oxidation step in dry atmospheres is thought to be the rate limiting oxidation \(\text{BO}(g) + \text{O}_2(g) \rightarrow \text{BO}_2(g) + \text{O}(g)\), followed by the subsequent reaction of \(\text{BO}_2\) with additional BO molecules, the two step process producing \(\text{B}_2\text{O}_3\)(g). If BO(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 BO(g) nor solid boron but rather intermediate species. It has been suggested that one of these species might be \(\text{B}_2\text{O}\). If so, it is feasible that the process \(\text{B}_2\text{O}(g) + \text{O}_2(g)\) can compete with the two-step mechanism indicated above for \(\text{B}_2\text{O}_3\)(g) formation. It is up to the modern kinetist 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 $Ag_xO$ constituences 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\textsubscript{x}O (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\textsubscript{x}O system have now also sparked a collaborative extension to the corresponding Ag\textsubscript{x}S 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\textsubscript{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 M\textsubscript{x}(CO)\textsubscript{x} (1 \leq n \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 M\textsubscript{n}(CO)\textsubscript{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.
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 permit 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
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 visible 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 can excite 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 McDaniel, a researcher in the ceramics section at Argonne, it is too small for practical use but 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 chemistry went to Georgia Tech, claims, according to Alex McDaniel, a researcher in the ceramics section at Argonne. He points out that visible light lasers when developed will be easier to focus and will operate with simpler equipment.

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

Dr Gole points out that visible light lasers when developed will be easier to focus and will operate with simpler equipment. He points out that visible light lasers when developed will be easier to focus and will operate with simpler equipment.

As an electromagnet circles around 30 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 in diameter with two ground states. The metal oxide molecules which are highly excited 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 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. 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.

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 be easier to focus and will operate with simpler equipment.

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 McDaniel, a researcher in the ceramics section at Argonne, it is too small for practical use but when developed will be easier to focus and will operate with simpler equipment. Richard McDaniel, a researcher in the ceramics section at Argonne, pours liquid nitrogen on the motor.

Dr Gole and Richard McDaniel demonstrating their motor, powered by visible light lasers, using liquid nitrogen.
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 semiconductors 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 Photography session of the Medical Imaging II: Image Formation, Detection, Processing, and Interpretation conference in March in Newport Beach, CA. He was interviewed recently by David S. SPIE Technical Consultant.

What is multispectral imaging, to you, 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 near infrared.

Do you use a laser source?

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

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

The Cole group points out that these chemical lasers, developed in the Georgia Tech School of Physics, also make more...
Do you use a laser source?

Aronowitz: No, we use a white light source and a CCD camera with 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.

A: How did interest in this procedure arise?

Aronowitz: Back in the mid-70s, I became aware of some work that as published in the Proceedings of the SPIE by two researchers in Arizona—Victor Anselmo, of the Jet Propulsion Laboratory, and Bruce Zawacki, a burn surgeon in Los Angeles. Their first article showed that, by using photographic infrared light, they were able to detect amorphous regions on a burn wound which had no surface features. They saw a darker region on an infrared image of a burn on a child's back, and this was reported to be the first indication that a colorimetric analysis of a burn would be useful.

The ratios of red to infrared, red to green, 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.


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 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..."
Visible light chemical lasers (continued from page 1)

Visible light chemical lasers

We studied these chemical reactions,” Golè explains, “but Golè said visible lasers, once developed, will be easy to focus and operate with simpler equipment.

The optical system also includes Stephen H. Cobb and J. Robert Woodward, is attempting to convert the amplifier systems to laser oscillators. The two mutually discovered the chemical oscillators produce a green light, but Golè adds that additional research is 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 is high, an appreciable number of molecules is excited to the upper level of the two energy levels.

The continuous wave amplifier creates a population inversion by relaxing molecules excited to different levels. The excited state population is relaxed by the upper laser cavity, allowing the laser to operate continuously.

As the excited sodium molecules release light, they release their energy at one time, where they immediately react with excess bromine 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, Golè explains, is that the excited sodium (Na) molecules emit light at a rate that they can react with the excess bromine atoms. The pulse amplifier relies on the rapid transfer of energy from the 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 carbon. 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. They then 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 on its own, creating the necessary population inversion.

The search for chemically driven visible lasers has occupied researchers for two decades, Golè reports. “The number of approaches that have been taken attempts to make this laser work probably take about seven pages to list,” he added. “There have been many possibilities, but until now, they all had some flaws.”

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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 sub 3 ) with atoms of a halogen (chlorine, bromine, or iodine).

This reaction forms sodium halide molecules and molecules consisting of two sodium atoms (Na sub 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 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.

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 computation 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 $1 \times 10^{10}$ transistors.

In typical digital use, many of the
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 μm 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.
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. Ironi- cally, 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...
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.

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

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 trimmer, Na₃. Chlorine, bromine, or iodine atoms react with the Na₃ molecules to form a sodium halide and an excited sodium dimer, Na₂.
The highly exothermic reaction between the sodium molecules and halogen atoms in crossed beams produced bright fluorescence from Na₂ 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 10⁻² 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 depletes 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 7₁/₂ 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