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ENERGY TRANSFER AND OPTICAL SPECTROSCOPY OF DIATOMIC MOLECULES --ETC(U)  
DEC 79 H P BROIDA, D O HARRIS AFOSR-77-3138

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power, high operating efficiency and lower weight. Additionally, optically pumped metal dimers are attractive systems for visible, tunable gas lasers. The development of new improved chemical laser systems and optically pumped laser systems requires an increased understanding and knowledge of the properties and characteristics of candidate reactions and molecules.

Detailed spectroscopic studies on both  $CuF$  and  $Ca_2$  have been carried out. Use of laser photoluminescence has produced spectroscopic information previously unobtainable. We have obtained improved molecular constants and dissociation energies, radiative lifetimes, and quenching cross-sections for electronically excited products. In addition previously unknown electronic states have been identified. ←

Using spectroscopic information previously obtained in this laboratory, we have demonstrated that the  $Bi_2$  molecule can be used as an optically pumped laser. Other molecules have been investigated as optically pumped laser media without success: these include  $Rb_2$  and  $Ca_2$ .

An ultrahigh vacuum system with He recirculating cryogenic refrigerator has been constructed along with a bake-out oven, and an elaborate gas handling system. This system has been thoroughly tested and preliminary matrix isolation studies of  $N_2$  have been carried out.

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## FINAL REPORT

August 1976 - Dec 1979

Organization: AFOSR Project: 2303 Task: B1  
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Title: Energy Transfer and Optical Spectroscopy of Diatomic Molecules  
in Chemically Reacting Systems

- A. Dr. H. P. Broida, Principal Investigator  
Dr. David O. Harris, Principal Investigator  
B. Description of Effort  
(1) Abstract:

Increased capabilities in remote sensing, communication and several other areas depend on developments in laser technology. Chemical lasers indicate a high probability of fulfilling these needs through their properties of different wavelengths, high power, high operating efficiency and lower weight. Additionally, optically pumped metal dimers are attractive systems for visible, tunable gas lasers. The development of new improved chemical laser systems and optically pumped laser systems requires an increased understanding and knowledge of the properties and characteristics of candidate reactions and molecules.

Detailed spectroscopic studies on both CuF and Ca<sub>2</sub> have been carried out. Use of laser photoluminescence has produced spectroscopic information previously unobtainable. We have obtained improved molecular constants and dissociation energies, radiative lifetimes, and quenching cross-sections for electronically excited products. In addition previously unknown electronic states have been identified.

Using spectroscopic information previously obtained in this laboratory, we have demonstrated that the Bi<sub>2</sub> molecule can be used as an optically pumped laser. Other molecules have been investigated as optically pumped laser media without success: these include Rb<sub>2</sub> and Ca<sub>2</sub>.

An ultrahigh vacuum system with He recirculating cryogenic refrigerator has been constructed along with a bake-out oven, and an elaborate gas handling system. This system has been thoroughly tested and preliminary matrix isolation studies of N<sub>2</sub> have been carried out.

(2) Progress: a. CuF

A flow system designed for the study of reactions involving metal atoms has been used to study chemiluminescent CuF. Copper vapor produced in the system is reacted with F<sub>2</sub>, NF<sub>3</sub>, and SF<sub>6</sub> to produce visible emission. Spectral measurements of the chemiluminescent emission indicate excited state production efficiencies of 0.3% for Cu + F<sub>2</sub> and 0.1% for Cu + NF<sub>3</sub>. As much as 12% of the emission produced with NF<sub>3</sub> is from atomic copper. Previously unseen bands appearing in the strong chemiluminescence of Cu + F<sub>2</sub> include a violet system with T<sub>e</sub> = 21364 cm<sup>-1</sup> and ω<sub>e</sub> = 495 cm<sup>-1</sup> and two infrared bands with T<sub>e</sub> = 11380 and 11915 cm<sup>-1</sup> and with ω<sub>e</sub> = 580 cm<sup>-1</sup>. Comparison of the chemiluminescence with computer generated synthetic spectra has made possible the determination of excited state population distributions among the electronic, vibrational and rotational states.

To complement the chemiluminescence studies a flow system has been adapted for use with a computerized laser excitation system. Simultaneous measurements of the radiative lifetime, collisional quenching rate and spectral line positions are made by this system. Line positions are made relative to  $I_2$  reference lines to interferometric accuracy. A new value for  $B_0 = .3692$  and  $D_0 = 5.1 \times 10^{-1} \text{ cm}^{-1}$  for the  $B^1\Sigma$  state of  $\text{CuF}$  has been calculated from measured line positions. Radiative lifetimes for the A, B and C states have been measured to be  $7.3 \pm 0.1$ ,  $1.2 \pm 0.1$  and  $0.6 \pm 0.4 \text{ } \mu\text{sec}$  respectively. An argon quenching cross section of  $8.5 \times 10^{-17} \text{ cm}^2$  has been measured from the pressure dependence of the A state photoluminescence decay rate. These results have been published in Ref. 5.

#### b. $\text{Ca}_2$

A heat-pipe oven made of alumina ( $\text{Al}_2\text{O}_3$ ) has been constructed and tested with calcium metal. Temperatures of  $1400^\circ\text{C}$  have been achieved which correspond to total calcium vapor pressures of about 400 torr. Tests have shown that the calcium metal wets the alumina walls, eliminating the need for a wick. Since the alumina can be safely operated at temperatures as high as  $1600^\circ\text{C}$ , calcium vapor pressures over an atmosphere will be possible.

Bright laser photoluminescence is observed when calcium metal vapor is illuminated with laser light in the 620-660 nm region. The resultant molecular bands are assigned to  $\text{Ca}_2 B^1\Sigma_u^+ - X^1\Sigma_g^+$ . Observed by others in the matrix at  $4\text{-}10^\circ\text{K}$ , the X state must be the ground electronic state. The gas phase vibrational constants for X are found to be  $\omega_e^u > 73.18(+0.16)$ ,  $\omega_e x_e^u = 0.560(+0.010)$  and  $\omega_e y_e^u = -1.59 \times 10^{-3}(+0.17 \times 10^{-3}) \text{ cm}^{-1}$ . The dissociation energy is found to be  $D_0 > 2075(+150) \text{ cm}^{-1}$ . The previously assigned ground state has vibrational constants which significantly disagree with those found for X and is therefore reassigned to an excited electronic level,  $C^1\Sigma_g^+$ . The results of previous workers are in agreement with these assignments. The equilibrium vapor pressure at  $1400^\circ\text{K}$  of ground state calcium molecules is estimated to be  $\sqrt{5}$  torr. The results of this investigation are being prepared for publication (Ref. 7 and 9).

Long range energy levels are observed in  $\text{Ca}_2 C^1\Sigma_g^+$  using laser photoluminescence. Vibrational progressions are observed from  $v'' = 0$  to the dissociation limit for numerous J levels. Oscillatory continuum emission smoothly begins where the discrete vibrational levels end. At  $J = 28$ , thirty-three vibrational levels are observed to be bound, while only 26 levels are bound at  $J = 68$  and 7 levels at  $J = 161$ . At  $J > 210$ , no bound vibrational levels are observed. Rotational predissociation is observed in emission as both broadened and weakened spectral lines. Improved molecular constants are calculated to be  $\omega_e = 64.5969 (+0.0036)$ ,  $\omega_e x_e = 1.0461 (+0.0003)$ ,  $\omega_e y_e = 2.5618 \times 10^{-3} (+5.2 \times 10^{-6})$ ,  $B_e = 4.5855 \times 10^{-2} (+7.6 \times 10^{-6})$ ,  $\alpha_e = 6.4738 \times 10^{-4} (+9.6 \times 10^{-7})$  and  $\gamma_e = -8.9362 \times 10^{-6} (+3.1 \times 10^{-8}) \text{ cm}^{-1}$ . From these values, classical RKR turning points are calculated and yield a potential energy curve which ranges from 2.4 - 12.1 Å. The long-range potential energy dependence is determined to be  $V = D_0 - C_5 r^{-5}$  where  $D_0$ , the dissociation energy, is found to be  $1068.8 (+2.3) \text{ cm}^{-1}$  ( $D_e = 1100.6 (+2.3) \text{ cm}^{-1}$ ) and  $C_5 = 1.18 (+0.10) \times 10^6 \text{ Å}^5 \text{ cm}^{-1}$ . The last

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bound vibrational level is estimated to be  $v_D = 44 + 2$ . An  $r^{-5}$  long-range dependence is expected from two atoms whose electronic angular momentum is separated by 2, such as S + D or P + F. The C state is therefore reassigned from  $^1S + ^1S$  atoms to a  $^1\Sigma_g^+$  state which correlates with  $^1S + ^1D$  atoms. The work is to be presented in Refs. 7 and 8.

Laser induced fluorescence has recently been observed from  $Ag_2$  molecules in a high temperature ceramic heat pipe. The emission is in the A-X system of the silver dimers and is observed with both  $Ar^+$  laser and flash lamp pumped dye laser excitation. The  $Ag_2$  molecule appears to be a good candidate for an optically pumped laser, pumping at  $\sim 4000\text{\AA}$  and lasing at  $\sim 4800\text{\AA}$ .

#### c. Optically pumped molecular lasers

Laser emission, attributed to  $Bi_2$  molecules, has been observed between 650 and 710 nm, the region of  $Bi_2$  A-X emission. Bismuth vapor was optically pumped, using a flashlamp pumped dye laser, in the A-X absorption bands between 540 and 580 nm. A 0.2% efficiency of this laser was found. These results have been published in Ref. 6.

In addition two other molecules have been investigated as optically pumped laser media,  $Ca_2$  and  $Rb_2$ . As of this writing, neither of these have proven successful. Following extensive efforts with  $Ca_2$ , further spectroscopic work indicated that lower level of the electronic transition of  $Ca_2$  with which we were working was not the ground state. Because of this, the population of this level in the cell was probably much too low. The reasons for failure with  $Rb_2$  are not certain and further spectroscopic work would be useful.

#### d. Molecule-metal surface interactions

Construction of an ultrahigh vacuum (UHV) system designed to spectroscopically study molecule-surface interactions is now complete. Testing of equipment has been concurrent with assembly and the diagnostic experiments are now being carried out.

This UHV system is unique in that it not only obtains a lower pressure of about  $5 \times 10^{-11}$  torr after bakeout, but also has a substrate whose temperature can be maintained at any temperature between 15K and 300K to within 0.1K. The helium recirculating refrigerator which cools the substrate is completely bakeable to 200°C, as is the rest of the UHV system. The variable temperature substrate is centrally located so that it faces two evaporation furnaces for depositing metals on the substrate. The system incorporates a 0 - 300 a.m.u. mass analyzer with better than 1 a.m.u. resolution, an ion gun for cleaning the surface, a 20 - 3000eV auger electron gun for exciting molecules on the surface, a shutter for shielding the cold substrate and two quartz windows, one for excitation by white light or laser and the other for observation with monochromator PMT and a dedicated data acquisition system. Additional ports are also available. The UHV system has two gas inlets with variable leak valves connected to an elaborate, bakeable diffusion pumped gas handling system. It will be possible to study a wide range of surface-molecule interactions with this versatile system.

Recently, studies of atomic  $N^{2D-4S}$  emission following electron bombardment of solid  $N_2$  have been begun. Molecular  $N_2$  is deposited on a 15K silver surface, and the thickness of the solid  $N_2$  is controlled by the depo-

sition pressure and time. The  $N^2D^+4S$  has an observed lifetime of 37 sec. for  $N_2$  thicknesses  $\geq 6000\text{\AA}$  in agreement with previously published values. However, as the thickness of the  $N_2$  layer is decreased, the lifetime becomes much shorter. This result is in qualitative agreement with previously published experimental and theoretical work on more complicated molecular systems. These results are most exciting and further work is in progress.

Along with the UHV surface work, there has also been some rare gas matrix isolation spectroscopy done in a conventional diffusion pumped-liquid Helium dewar high vacuum system. This "dirty" system was used to find molecules and excitation methods which yield high quantum efficiencies in the desired spectral region. Besides being a useful prototype of the UHV system it has also yielded information on excitation and decay (both radiative and non-radiative) of molecular states in both rare gas matrices and the pure solid. For example an electronic transition of CO not previously observed in matrix isolation spectroscopy has been seen in an Ar matrix using 58.4 nm photoexcitation.

#### AFOSR Supported Publications

1. C. Linton                      Flame Spectroscopy of TiO: Chemiluminescence  
H. P. Broida                    J. Mol. Spectrosc. 64, 382-8 (1977).
2. C. Linton                      Flame Spectroscopy of TiO: Photoluminescence  
H. P. Broida                    of the  $\alpha(C^3\Delta - X^3\Delta)$  System  
J. Mol. Spectrosc. 64, 389-400 (1977).
3. R. E. Steele                  Flame Spectroscopy of TiO: Radiative Lifetimes and  
C. Linton                        Oscillator Strengths of the  $\alpha(C^3\Delta - X^3\Delta)$  System  
J. Mol. Spectrosc. 69, 66-70 (1978).
4. R. E. Steele                  Chemiluminescence, Photoluminescence and Radiative  
Lifetimes of Diatomic Copper Fluoride  
Ph.D. Thesis, University of California, Santa Barbara  
October 1977.
5. R. E. Steele                  Chemiluminescent and Excitation Spectra of CuF  
H. P. Broida                    Journal of Chemical Physics 69, 2300-2305 (1978).
6. W. P. West                    Optically Pumped Vapor Phase  $Bi_2$  Laser  
H. P. Broida                    Chemical Physics Letters 56, 283-285 (1978).
7. J. C. Wyss                    Photoluminescence of Calcium Molecules  
Ph.D. Thesis, University of California, Santa Barbara  
December 1978.
8. J. C. Wyss                    Long Range Energy Levels of  $Ca_2$ , in preparation for  
R. Belanger                    submission to J. Chem. Phys.  
H. P. Broida
9. J. C. Wyss                    Calcium Molecules -- A New Ground State, in preparation  
for submission to J. Chem. Phys.

10. "Luminescence and Nonradiative Energy Transfer to Surfaces", A. Adams, R.W. Rendell, W.P. West, H.P. Broida, P.K. Hansma and H. Metiu, Phys. Rev. B (scheduled June 15, 1980).
11. "Effect of Metal Film Thickness on Surface-Atom Coupling", A. Adams, R.W. Rendell, R.W. Garnett, P.K. Hansma and H. Metiu, Optics Communications (Amsterdam, submitted May, 1980).
12. "Practical Range and Energy Loss of 0.1-3 keV Electrons in Thin Films of N<sub>2</sub>, O<sub>2</sub>, A, Kr and Xe", A. Adams and P.K. Hansma, Phys. Rev. B (submitted May, 1980).
13. "Nonradiative Energy Transfer from Atoms to Surface Plasmons", A. Adams, dissertation, University of California at Santa Barbara (May, 1980).

## AFOSR supported Talks and Presented Papers

1. "Possible Visible Chemical Lasers, Sigma Xi, Washington D.C. Chapter, (H. P. Broida), December 4, 1976.
2. "Chemiluminescence and Photoluminescence of Gas Phase CuF" American Physical Society, Winter Meeting, Stanford, CA (R. E. Steele) December 21, 1976.
3. "Chemiluminescence and Photoluminescence of Metal Atom Reactions" Bell Laboratory, Murray Hill, N. J. (H. P. Broida) January 31, 1977.
4. "Molecular Physics Research at UCSB" Molecular Physics Section, National Bureau of Standards, Gaithersburg, MD (H. P. Broida) February 2, 1977.
5. "Chemiluminescence and Photoluminescence of Metal Atom Reactions" Chemistry Seminar, M.I.T., Cambridge, MA (H. P. Broida) February 8, 1977.
6. "Surface Chemiluminescence in Ultra-high Vacuum Systems" Surface Science Group, National Bureau of Standards, Gaithersburg, MD (H. P. Broida) February 14, 1977.
7. "Chemiluminescence and Photoluminescence of Metal Atom Reactions" Naval Research Laboratory, Washington, D.C. (H. P. Broida) March 10, 1977.
8. "Chemiluminescence and Photoluminescence of Metal Atom Reactions" Chemistry Department, University of Virginia, Charlottesville, VA (H. P. Broida) April 8, 1977.
9. "Chemiluminescence and Photoluminescence of Metal Atom Reactions" Theoretical Chemistry Institute, University of Wisconsin, Madison, WI (H. P. Broida) May 13, 1977.
10. "Photoluminescence of Gas Phase Calcium Dimer Molecules" American Physical Society, Winter Meeting, San Francisco, CA (J. C. Wyss) January, 1978.
11. "The Bi<sub>2</sub> Optical Transfer Laser" General Motors Research Laboratories, Warren, MI (W. P. West) February, 1978.
12. "Dissociation Energy of Calcium Molecules" 33rd Symposium on Molecular Spectroscopy, Columbus, Ohio (J. C. Wyss and H. P. Broida) June, 1978.
13. "58.4 nm Photon Excitation of Solid and Matrix Isolated N<sub>2</sub>" 33rd Symposium on Molecular Spectroscopy, Columbus, Ohio (A. Adams and H. P. Broida) June, 1978.
14. "Optically Pumped Bi<sub>2</sub> Molecular Laser" Varian Instruments, Palo Alto, CA (W. P. West) August, 1978.
15. "The Bi<sub>2</sub> Optically Pumped Molecular Laser" Rocketdyne, Canoga Park, CA (W. P. West) August, 1978.