

AD-A064 425

UNIVERSITY OF SOUTHERN CALIFORNIA LOS ANGELES DEPT O--ETC F/6 7/5
PULSED INFRARED LASER INDUCED VISIBLE LUMINESCENCE.(U)

JAN 79 G E HARDY, A P CHANDRA, J I ZINK

N00041-76-C-0548

UNCLASSIFIED

TR-6

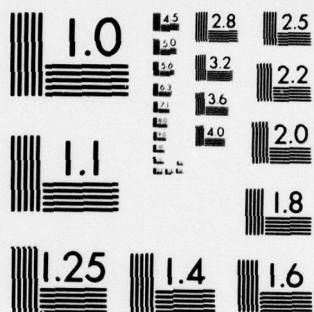
NL

OF
AD
A064425



END
DATE
FILMED
4 -79

DDC



MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS
BEFORE COMPLETING FORM

1. REPORT NUMBER (6) 61	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER (12) (14) TR-6
4. TITLE (and Subtitle) Pulsed Infrared Laser Induced Visible Luminescence		5. TYPE OF REPORT & PERIOD COVERED (9) Technical Report, #6, 1978
6. PERFORMING ORG. REPORT NUMBER (10)		7. CONTRACT OR GRANT NUMBER(s) (15) N00014-76-C-0548
9. PERFORMING ORGANIZATION NAME AND ADDRESS University of Southern California Department of Chemistry Los Angeles, California 90007		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR 051-609
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research (Code 472) Arlington, Va. 22217		12. REPORT DATE (11) Jan 1979
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		13. NUMBER OF PAGES (12) 13p.
LEVEL		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approved for Public Release; Distribution Unlimited		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) triboluminescence luminescence laser induced luminescence laser J/sq. cm		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Crystals of saccharin doped with p-toluenesulfonamide, coumarin, NaCl, and KCl are found to emit in the visible, following a 20 nsec pulse of high intensity 1060 nm radiation. The pulses were 0.5 to 4 J cm ² in energy, corresponding to up to 200 MW peak power. The emissions in the first two cases are from molecular excited states, but with differences in detail from those induced by photoexcitation or found in triboluminescence. NaCl and KCl show neither photoemission or relevant triboluminescence, and the laser induced emission is (continued)		

DD FORM 1 JAN 73 1473

EDITION OF 1 NOV 65 IS OBSOLETE
S/N 0102-LF-014 6601

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

361555

79

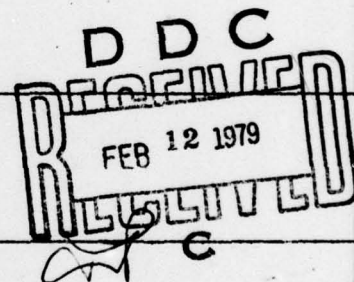
02

05

009

ADA064425

DDC FILE COPY



20. Abstract (continued)

essentially that found thermally or by mechanically stressing x- or γ -ray irradiated crystals. It is attributed to electron-hole recombination. The mechanism of the laser induced emission may thus involve some combination of mechanical shock wave and of plasma ionization. The trivial explanations of photoexcitation by higher harmonics of the 1060 nm fundamental or through successive multiple photon processes can be ruled out.

ACCESSION for

NTIS	White Section	☒
DOC	G. H. Section	☐
UNCLASSIFIED		☐
DISSEMINATION/AVAILABILITY CODES		
A		

79 02 05 009

OFFICE OF NAVAL RESEARCH

Contract N00014-76-C-0548

TECHNICAL REPORT NO. 6

Pulsed Infrared Laser Induced Visible Luminescence

by

G. E. Hardy, B. P. Chandra, and Jeffrey I. Zink*

Department of Chemistry
University of California Los Angeles
Los Angeles, California 90024

Arthur W. Adamson*, R. Fukuda, and R. T. Walters

Department of Chemistry
University of Southern California
Los Angeles, California 90007

Prepared for Publication

in the

Journal of the American Chemical Society

January, 1979

Reproduction in whole or in part is permitted for
any purpose of the United States Government

Approved for Public Release; Distribution Unlimited.

Abstract

Pulsed Infrared Laser Induced Visible Luminescence

G. E. Hardy, B. P. Chandra, and Jeffrey I. Zink*

Department of Chemistry
University of California Los Angeles
Los Angeles, California 90024

Arthur W. Adamson*, R. Fukuda, and R. T. Walters

Department of Chemistry
University of Southern California
Los Angeles, California 90007

Crystals of saccharin doped with p-toluenesulfonamide, coumarin, NaCl, and KCl are found to emit in the visible, following a 20 nsec pulse of high intensity 1060 nm radiation. The pulses were 0.5 to 4 J cm^{-2} in energy, corresponding to up to 200 MW peak power. The emissions in the first two cases are from molecular excited states, but with differences in detail from those induced by photoexcitation or found in triboluminescence. NaCl and KCl show neither photoemission nor relevant triboluminescence, and the laser induced emission is essentially that found thermally or by mechanically stressing x- or γ -ray irradiated crystals. It is attributed to electron-hole recombination. The mechanism of the laser induced emission may thus involve some combination of mechanical shock wave and of plasma ionization. The trivial explanations of photoexcitation by higher harmonics of the 1060 nm fundamental or through successive multiple photon processes can be ruled out.

Pulsed Infrared Laser Induced Visible Luminescence

Sir:

Triboluminescence (TL) can be excited by fracturing or grinding a crystal, or by subjecting it to thermal shock.¹⁻³ We have been interested in whether comparable phenomena could be made to occur using a high energy laser pulse as the stress inducing agent. We report here on three cases in which there is luminescence induced by a 20 nsec, 1060 nm pulse from a Nd glass laser system,⁴ the pulse energies ranging from 0.5 to 4 J cm⁻² (about 200 MW peak power). The crystals were all single crystals in appearance, several mm in each dimension, and were studied at room temperature, ca. 24°C.

Figure 1a shows the laser induced luminescence spectrum for saccharin; it is the same within our resolution as the TL and photoluminescence (PL) spectra. The emission is actually from p-toluenesulfonamide impurity normally present in saccharin; such doped saccharin crystals are among the more intensely triboluminescent materials observed in our laboratory,⁵ hence this initial choice. The laser induced emission (LIE) showed two time regimes, as followed at 480 nm: a prompt emission and a longer lived one whose decay fit an exponential of about 300 nsec lifetime. From separate optical excitation experiments, the 480 nm emission has a lifetime of 57 psec at 77 K. The prompt component of the laser induced emission could represent ordinarily decaying excited states, but the 300 nsec component must have some other explanation, as discussed further below. The intensity of the 300 nsec emission was proportional to the laser pulse energy over about a ten fold range.

Substantial differences exist between the laser induced emission and TL spectra of coumarin. The LIE spectrum shown in Figure 1b consists of three peaks at 430, 475, and 505 nm. At room temperature, the PL and TL spectra of coumarin consist of a broad band centered at about 400 nm, which has been assigned as a $\pi \leftarrow \pi^*$ fluorescence.^{7,8} At 77 K, the PL spectrum consists of the fluorescence and a highly structured phosphorescence. The LIE of coumarin most closely resembles the lower temperature PL spectrum, with the most prominent peaks at 474 nm and 505 nm arising from $\pi \leftarrow \pi^*$ phosphorescence. The time dependence of the peaks follows the expected behavior. As the delay time between the laser pulse and the LIE measurement was decreased from 80 nsec to zero, the intensity of the fluorescence at 430 nm increased relative to that of the phosphorescence.

The laser induced emissions of NaCl and KCl consist of broad bands centered around 380 nm and 470 nm, respectively, as shown in Figure 1c. Neither crystal is photoluminescent with visible or u.v. excitation, or triboluminescent in this spectral region. However, x- or γ -ray irradiated crystals show both TL and thermoluminescence.⁹ The emission is due to recombination of displaced electrons with lattice atoms or ions. The emission spectra vary with crystal preparation and history, and with excitation method and temperature. Thus for NaCl, reported emission maxima range from 350 nm to 420 nm, and those for KCl, from 400 nm to 440 nm.^{9,10} Our laser induced emissions match the above characteristics.

Certain trivial explanations of our observations can be ruled out. Ordinary photoluminescence can be eliminated, of course, on energetic grounds. Nor is there any evidence for PL via higher harmonic generation. Neither 530 nm nor 353 nm scatter was observed. Also, successive multiphoton

absorption can be eliminated in the case of saccharin since the emission intensity was linear in laser pulse energy.

We can suggest two possibly important mechanisms: mechanical stress and electron-hole recombination. It is known, for example, that laser pulses such as used here can produce pressure waves reaching kilobar levels.¹¹⁻¹³ A possibility, then, is one of laser shock induced triboluminescence. This could be the case with the doped saccharin. The spectra of the LIE and TL molecular emissions are essentially the same. The 300 nsec emission decay in the former case is about what would be expected were a fan of shock-induced stress concentrations, or of actual cracks, propagating through the crystal at the speed of sound (with attenuation). The crystals all tended to crack or spall on successive laser shots. Note, however, that the laser induced emission differs from triboluminescence in that no excited state N_2 emission occurs.

The mechanical stress explanation also suffers in the case of coumarin since the TL spectrum shows only molecular fluorescence, while the LIE shows both fluorescence and phosphorescence. The cases of NaCl and of KCl are quite clearly unrelated to triboluminescence--there is none giving such emissions. Thus laser shock induced mechanical stress waves may account for some of the observations, but not for all of them.

Surface effects, such as the production of surface plasma may play a role in the excitation.¹² The intense laser beam could produce electron-hole pairs and an associated pressure or heat wave might then induce electron recombination with consequent emission. Although the mechanism is uncertain at present, our results clearly indicate that intense IR pulses can excite molecular fluorescence, molecular phosphorescence, and alkali metal halide defect emission.

The phenomena are under continuing investigation. Preliminary indications are that pulsed laser induced emission occurs with other crystalline materials. A partial list includes $\text{BaPt}(\text{CN})_4$, europium(III) chelates, uranyl nitrate, phenanthrene, phthalic anhydride, and chlorotriphenylmethane.

Acknowledgements

These investigations were supported in part by a grant from the U. S. Army Research Office (Durham) to the University of California Los Angeles, and by a contract between the U. S. Office of Naval Research and the University of Southern California. One of us (B. P. C.) is grateful to the Indian Ministry of Education and Social Welfare for a National Scholarship. The assistance of J. Tse in the initial observations is gratefully acknowledged.

References and Notes

- (1) J. I. Zink, *Accounts Chem. Res.*, 11, 289 (1978).
- (2) J. I. Zink and W. C. Kaska, *J. Am. Chem. Soc.*, 95, 7510 (1973).
- (3) F. G. Wick, *J. Opt. Soc. Amer.*, 29, 275 (1939).
- (4) See A. R. Gutierrez and A. W. Adamson, *J. Phys. Chem.*, 82, 902 (1978).

The time resolved spectra of Figure 1b were obtained with the use of a silicon intensified (SIT) vidicon detector and multichannel analyzer from Princeton Applied Research.

- (5) G. E. Hardy, B. P. Chandra, and J. I. Zink, unpublished results.
- (6) G. E. Hardy, J. C. Baldwin, J. I. Zink, W. C. Kaska, P. H. Liu, and L. Dubois, *J. Am. Chem. Soc.*, 99, 3553 (1977).
- (7) P. S. Song and W. H. Gordon, *J. Phys. Chem.*, 74, 4243 (1970).
- (8) W. W. Mantulin and P. S. Song, *J. Am. Chem. Soc.*, 95, 5122 (1973).

- (9) C. T. Butler, Phys. Rev., 141, 750 (1966).
- (10) (a) A. Halperin, N. Kristianpoller, and A. Ben-Zvi, Phys. Rev., 116
1081, (1959).
(b) A. Halperin, and N. Kristianpoller, J. Opt. Soc. Amer., 48, 996 (1958).
- (11) J. D. O'Keefe, C. H. Skeen, and C. M. York, J. Appl. Phys., 44,
4622 (1973).
- (12) T. J. Magee, R. A. Armistead, and P. Krehl, J. Phys. D: Appl. Phys.,
8, 498 (1975).
- (13) L. C. Yang, J. Appl. Phys., 45, 2601 (1974).

G. E. Hardy, B. P. Chandra, and Jeffrey I. Zink*

Department of Chemistry
University of California Los Angeles
Los Angeles, California, 90024

Arthur W. Adamson*, R. Fukuda, and R. T. Walters,

Department of Chemistry
University of Southern California
Los Angeles, California, 90007

Figure legend:

Figure 1. Spectra. 1a. p-toluenesulfonamide doped saccharin. Full line: triboluminescence spectrum (the short wavelength, structured emission is due to excited state N_2).⁶ Dashed line: laser induced emission. (Both measurements at room temperature; the 480 nm peaks are normalized). 1b. Coumarin. Full lines: laser induced emission, curve 1 with no delay, and curve 2 with 80 nsec delay. Dashed line: 353 nm photoexcited emission at 77 K (at room temperature, only the 420 nm centered emission is observed). (The intensity scale is arbitrary, and the spectra are roughly normalized; they are uncorrected). 1c. Laser induced emissions from NaCl, curve 1, and KCl, curve 2.

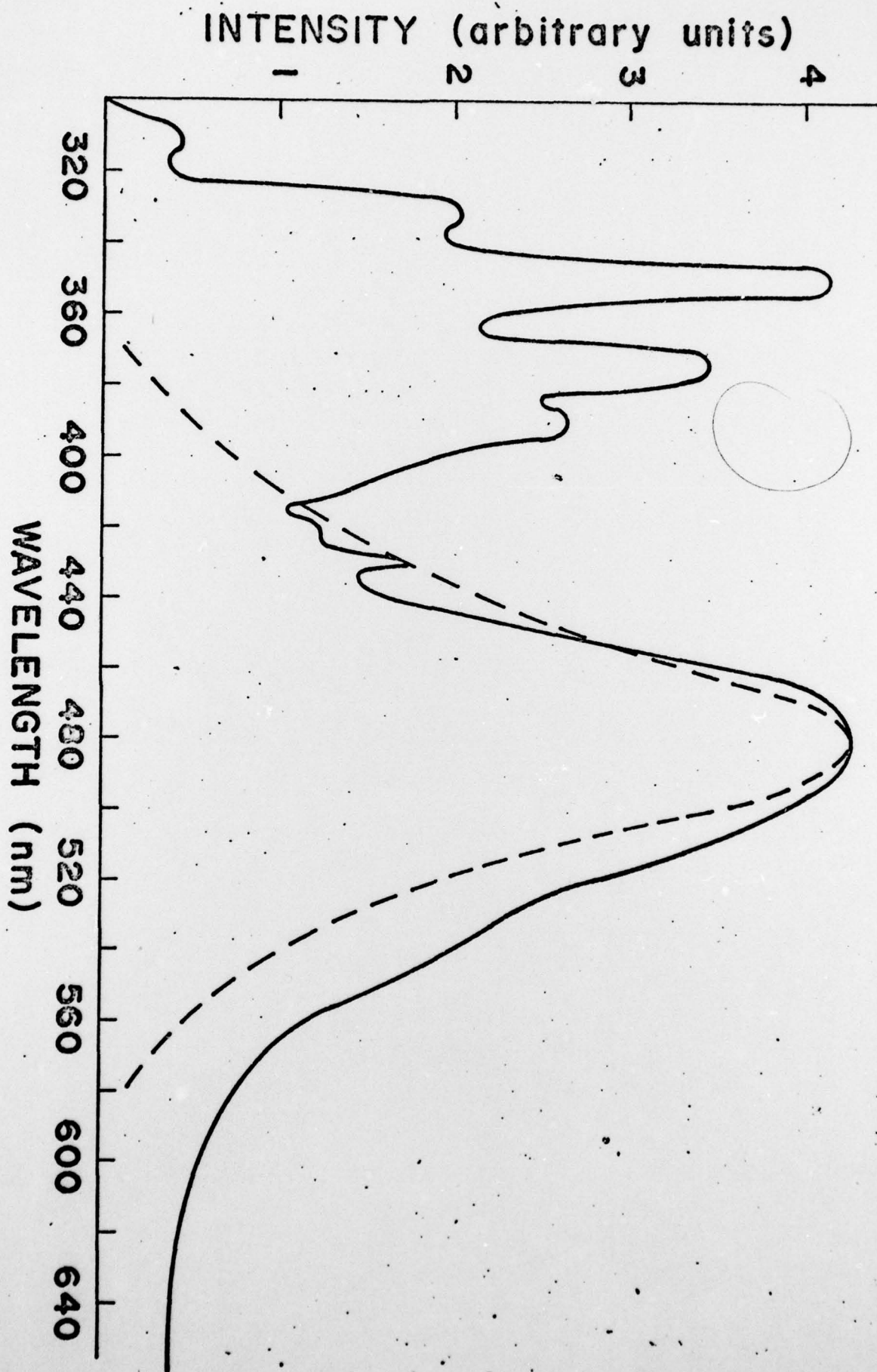


Fig 1a

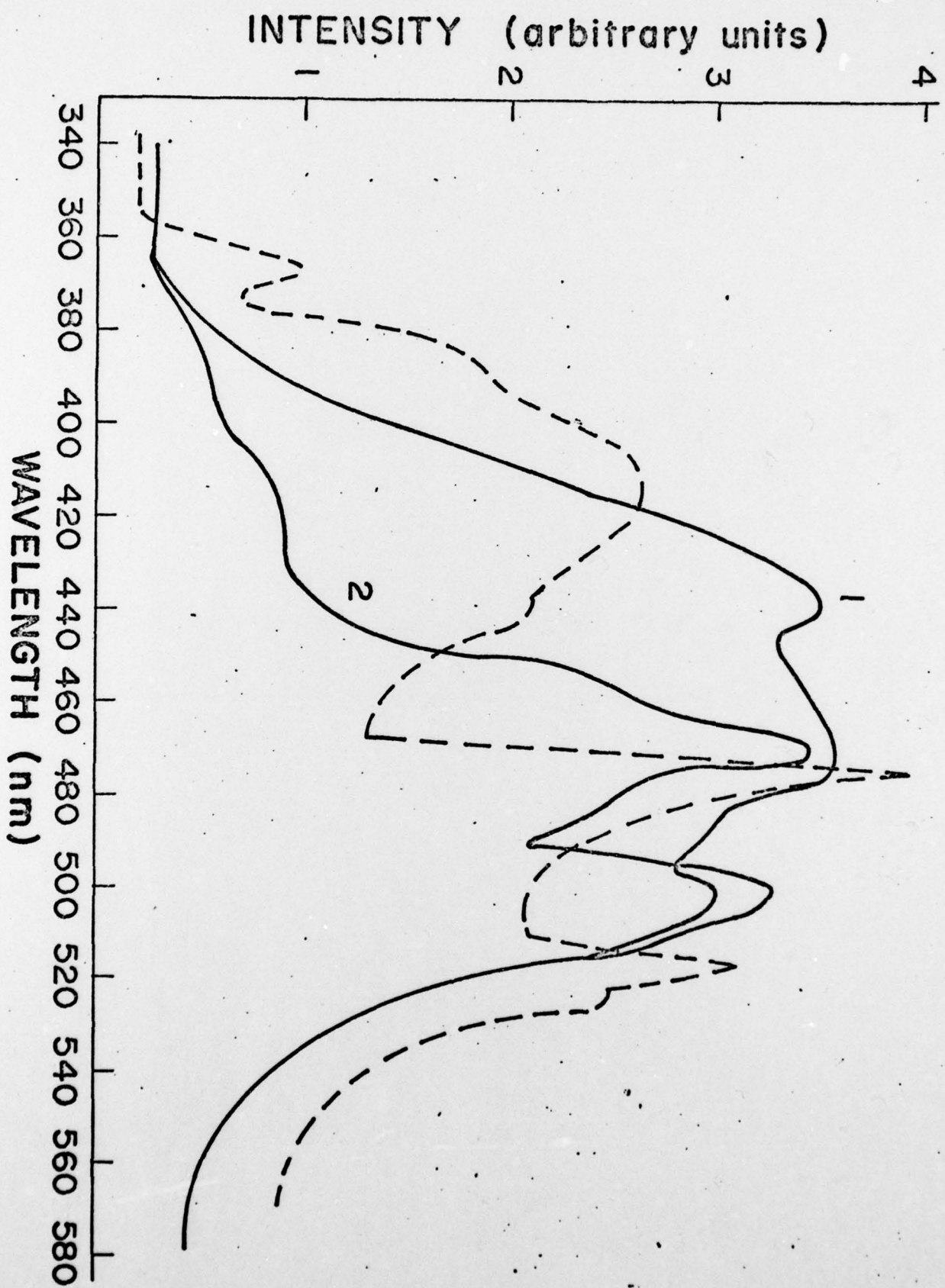


Fig. 1b

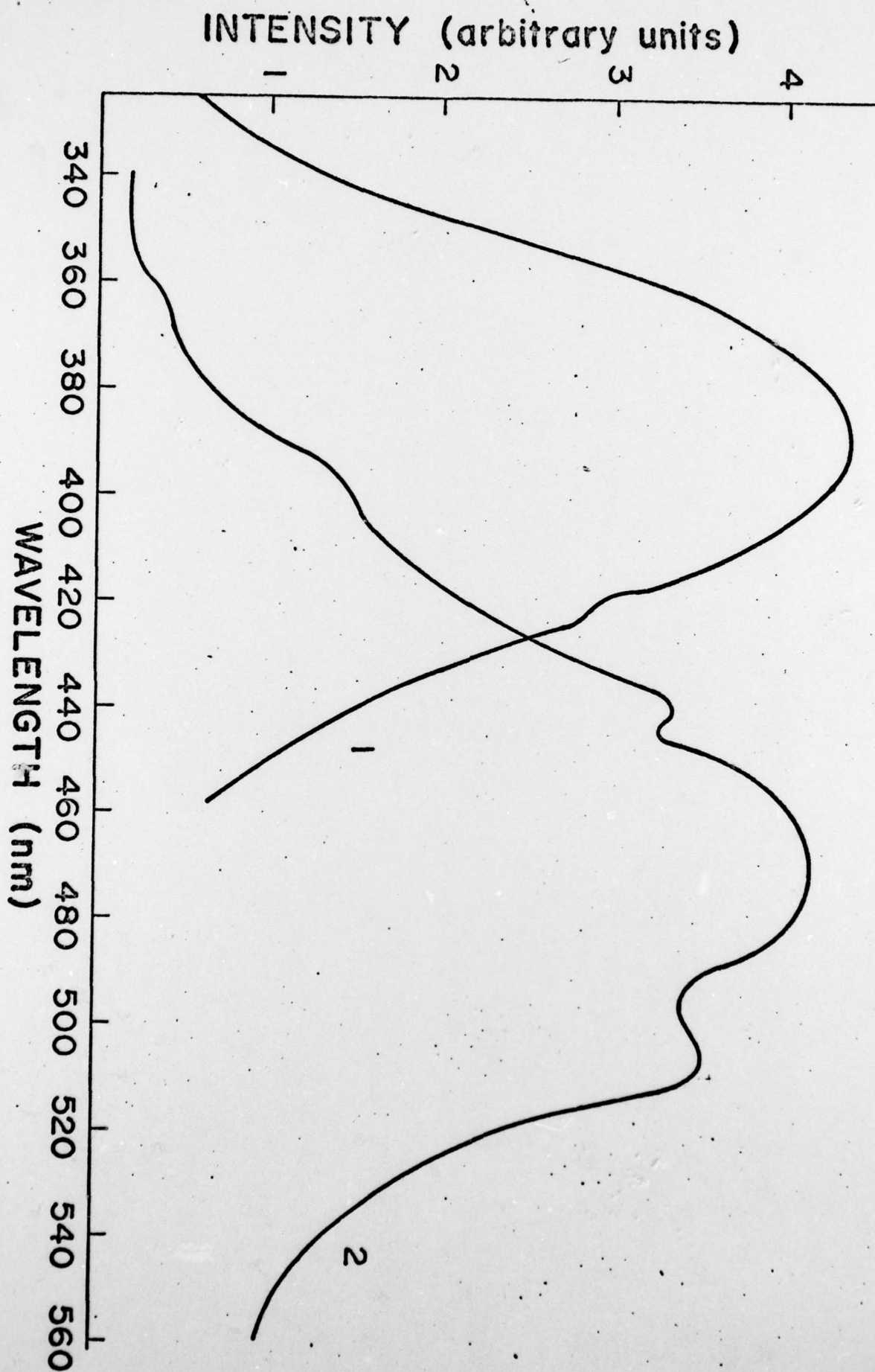


Fig. 1c

TECHNICAL REPORT DISTRIBUTION LIST

	<u>No. Copies</u>		<u>No. Copies</u>
Office of Naval Research Arlington, Virginia 22217 Attn: Code 472	2	Defense Documentation Center Building 5, Cameron Station Alexandria, Virginia 22314	12
Office of Naval Research Arlington, Virginia 22217 Attn: Code 102IP	1	U.S. Army Research Office P.O. Box 12211 Research Triangle Park, N.C. 27709 Attn: CRD-AA-IP	1
ONR Branch Office 536 S. Clark Street Chicago, Illinois 60605 Attn: Dr. Jerry Smith	1	Naval Ocean Systems Center San Diego, California 92152 Attn: Mr. Joe McCartney	1
ONR Branch Office 715 Broadway New York, New York 10003 Attn: Scientific Dept.	1	Naval Weapons Center China Lake, California 93555 Attn: Head, Chemistry Division	1
ONR Branch Office 1030 East Green Street Pasadena, California 91106 Attn: Dr. R. J. Marcus	1	Naval Civil Engineering Laboratory Port Hueneme, California 93041 Attn: Mr. W. S. Haynes	1
ONR Branch Office 760 Market Street, Rm. 447 San Francisco, California 94102 Attn: Dr. P. A. Miller	1	Professor O. Heinz Department of Physics & Chemistry Naval Postgraduate School Monterey, California 93940	1
ONR Branch Office 495 Summer Street Boston, Massachusetts 02210 Attn: Dr. L. H. Peebles	1	Dr. A. L. Slafkosky Scientific Advisor Commandant of the Marine Corps (Code RD-1) Washington, D.C. 20380	1
Director, Naval Research Laboratory Washington, D.C. 20390 Attn: Code 6100	1	Office of Naval Research Arlington, Virginia 22217 Attn: Dr. Richard S. Miller	1
The Asst. Secretary of the Navy (R&D) Department of the Navy Room 4E736, Pentagon Washington, D.C. 20350	1		
Commander, Naval Air Systems Command Department of the Navy Washington, D.C. 20360 Attn: Code 310C (H. Rosenwasser)	1		

TECHNICAL REPORT DISTRIBUTION LIST

	<u>No. Copies</u>		<u>No. Copies</u>
Dr. M. A. El-Sayed University of California Department of Chemistry Los Angeles, California 90024	1	Dr. G. B. Schuster University of Illinois Chemistry Department Urbana, Illinois 61801	1
Dr. M. W. Windsor Washington State University Department of Chemistry Pullman, Washington 99163	1	Dr. E. M. Eyring University of Utah Department of Chemistry Salt Lake City, Utah 84112	1
Dr. E. R. Bernstein Colorado State University Department of Chemistry Fort Collins, Colorado 80521	1	Dr. A. Adamson University of Southern California Department of Chemistry Los Angeles, California 90007	1
Dr. C. A. Heller Naval Weapons Center Code 6059 China Lake, California 93555	1	Dr. M. S. Wrighton Massachusetts Institute of Technology Department of Chemistry Cambridge, Massachusetts 02139	1
Dr. M. H. Chisholm Princeton University Department of Chemistry Princeton, New Jersey 08540	1	Dr. M. Rauhut American Cyanamid Company Chemical Research Division Bound Brook, New Jersey 08805	1
Dr. J. R. MacDonald Naval Research Laboratory Chemistry Division Code 6110 Washington, D.C. 20375	1		