

AD-A106 938

HOWARD UNIV WASHINGTON DC DEPT OF CHEMISTRY F/G 7/4  
MODEL ANALYSIS OF THE RAMAN SPECTRUM FROM FUSED SILICA OPTICAL --ETC(U)  
OCT 81 G E WALRAFEN, P N KRISHNAN N00014-80-C-0305

UNCLASSIFIED

TR-5

NL

10/1  
20/10/10



END

DATE

FORMED

42-811

DTIC

**LEVEL II**

**REPORT DOCUMENTATION PAGE**

READ INSTRUCTIONS  
BEFORE COMPLETING FORM

1. REPORT NUMBER <b>5</b>		2. GOVT ACCESSION NO. <b>AD-A106938</b>		3. RECIPIENT'S CATALOG NUMBER <b>(14) TR-5</b>	
4. TITLE (and Subtitle) <b>Model Analysis of the Raman Spectrum from Fused Silica Optical Fibers,</b>				5. TYPE OF REPORT & PERIOD COVERED <b>9 Technical Report 15, 1981</b>	
6. AUTHOR(s) <b>G. E. Walrafen and P. N. Krishnan</b>				7. PERFORMING ORG. REPORT NUMBER <b>NO014-80-C-0305</b>	
8. PERFORMING ORGANIZATION NAME AND ADDRESS <b>Chemistry Department Howard University Washington D. C. 20059</b>				9. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS <b>NR 051-733</b>	
10. CONTROLLING OFFICE NAME AND ADDRESS <b>Office of Naval Research Arlington, Va 22217</b>				11. REPORT DATE <b>Oct 1981</b>	
12. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)				13. NUMBER OF PAGES <b>12</b>	
				14. SECURITY CLASS (of this report)	
				15. 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)  
**DTIC ELECTE**  
**NOV 10 1981**

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)  
**Raman Spectrum, Optical Fibers, Fused Silica, Gaussian fit**

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)  
The Raman spectrum from pure silica optical fibers has been analyzed into a set of Gaussian components. Each component used is related to an observed feature of the spectrum, and a residual of about 1% resulted without the use of additional components. Both single- and multi-phonon peaks were fitted. These Gaussian components have analog in the infrared absorption spectrum, and hence they are of value in studying the fundamental and overtone infrared absorption of silica, as well as the infrared O<sub>n</sub> overtone and combination spectra.

**AD A106938**

**DTIC FILE COPY**

**81 10 27 273**

**"Model Analysis of the  
Raman Spectrum from  
Fused Silica Optical Fibers"**

by

**G. E. Walrafen and P. N. Krishnan\***  
**Chemistry Department**  
**Howard University**  
**Washington, D. C. 20059**

\* Visiting from the Department of Chemistry, Coppin State College,  
Baltimore, Maryland 21216

Accession For
PTIC GEAR
DTIC TAB
Unannounced
Justification
Re
Distribution/
Availability Codes
Avail and/or
Special

A

81 10 27 273

## ABSTRACT

The Raman spectrum from pure silica optical fibers has been analyzed into a set of Gaussian components. Each component used is related to an observed feature of the spectrum, and a residual of about 1% resulted without the use of additional components. Both single- and multi-phonon peaks were fitted. These Gaussian components have analogs in the infrared absorption spectrum, and hence they are of value in studying the fundamental and overtone infrared absorptions of silica, as well as the infrared OH overtone and combination spectra.

## INTRODUCTION

The Raman spectrum of fused silica is useful in elucidating its infrared absorption spectrum. Because the near-infrared absorption in silica fibers arises from overtones, combination tones, and tails from the fundamental infrared, an understanding of the silica infrared spectrum is of importance in determining the basic limits to transmission in optical fibers. By studying the Raman spectrum, features which may be weak and uncertain in the infrared can be confirmed. Even the important OH overtone absorptions include combinations involving silica infrared fundamentals. In a recent study of the OH overtone structure using a technique of Gaussian decomposition of the overtone absorption contours,<sup>(1)</sup> it was necessary in order to obtain consistent overtone structures, to invoke combination tones between OH overtones and silica infrared fundamentals which are relatively weak and unclear.

In this work we have used a similar analytical technique to resolve the Raman spectrum of fused silica (intensified by using long optical fibers) into a set of Gaussian components. This was accomplished using the strict constraint that only components correlated with a feature in the spectrum such as a peak, a shoulder, or a foot were employed. The resultant decomposition provided relative amplitudes and widths of the components. We have found that the Raman region between 0 and  $900\text{ cm}^{-1}$  could be fitted with a residual of 1% using only 10 components. One interesting result of this fit is that a weak fundamental infrared component used in explaining part of the OH overtone absorption spectrum was confirmed.<sup>(1)</sup> In the present work this component is

(2)

a major one, despite the fact that it appears only as a shoulder in the Raman spectrum.

Previously there has been only one attempt at decomposing the Raman contour from fused silica using a set of parabolas.<sup>(2)</sup> However, a different view of the structure of the Raman contour has generally prevailed. Theoretically, the depolarized Raman contour, when corrected for the Bose-Einstein thermal population factor, is the product of the density of states times the frequency dependent coupling coefficient, which involves Raman matrix elements.<sup>(3-5)</sup> The only reported computer decompositions using Gaussian components for fused silica have involved OH-stretching contours related to impurity OH.<sup>(6,7)</sup>

In the present work we applied Gaussian computer decomposition directly to the fundamental Raman spectrum from a pure (undoped) fused silica optical fiber, clad with silicone rubber, and 100  $\mu\text{m}$  in diameter.<sup>(8)</sup> The rationale for this procedure depends partly upon its success, although some justifications for it have been reported.<sup>(7)</sup> Of course, the use of components does not at all imply that the density of states view is incorrect. On the contrary, the present approach is seen as a possible method of subdividing the density of states according to specific contributions.

RESULTS AND DISCUSSION

In the present work the Raman spectrum from long fused silica optical fibers<sup>(9)</sup> was transferred to a straight horizontal baseline and deconvoluted using a DuPont 310 analog computer. The spectrum of fused silica and the results of our computer modelling of it are shown in Fig. 1 for the Raman region between 0 and  $900\text{ cm}^{-1}$ .

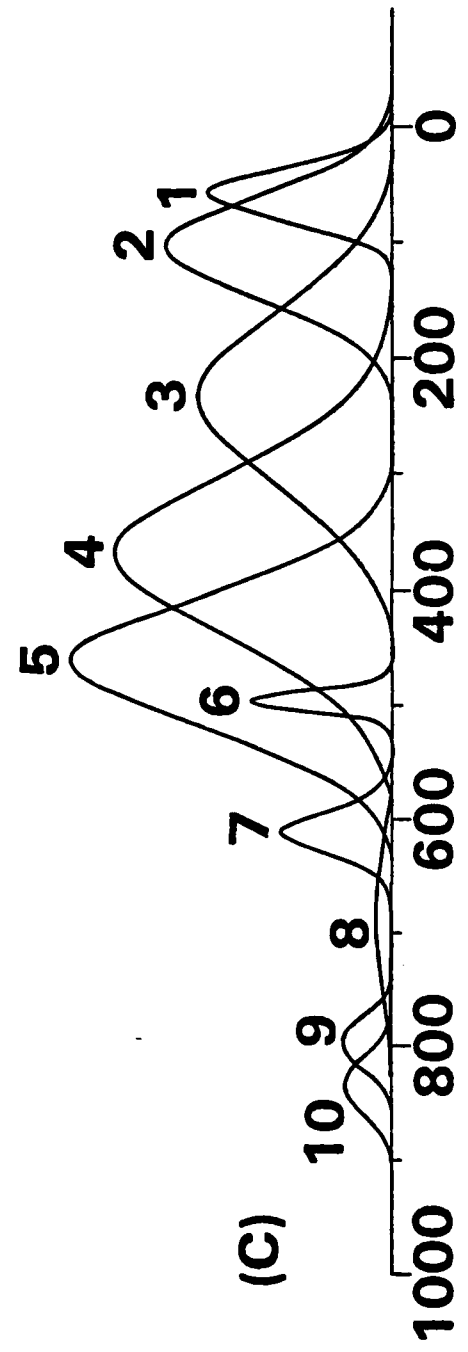
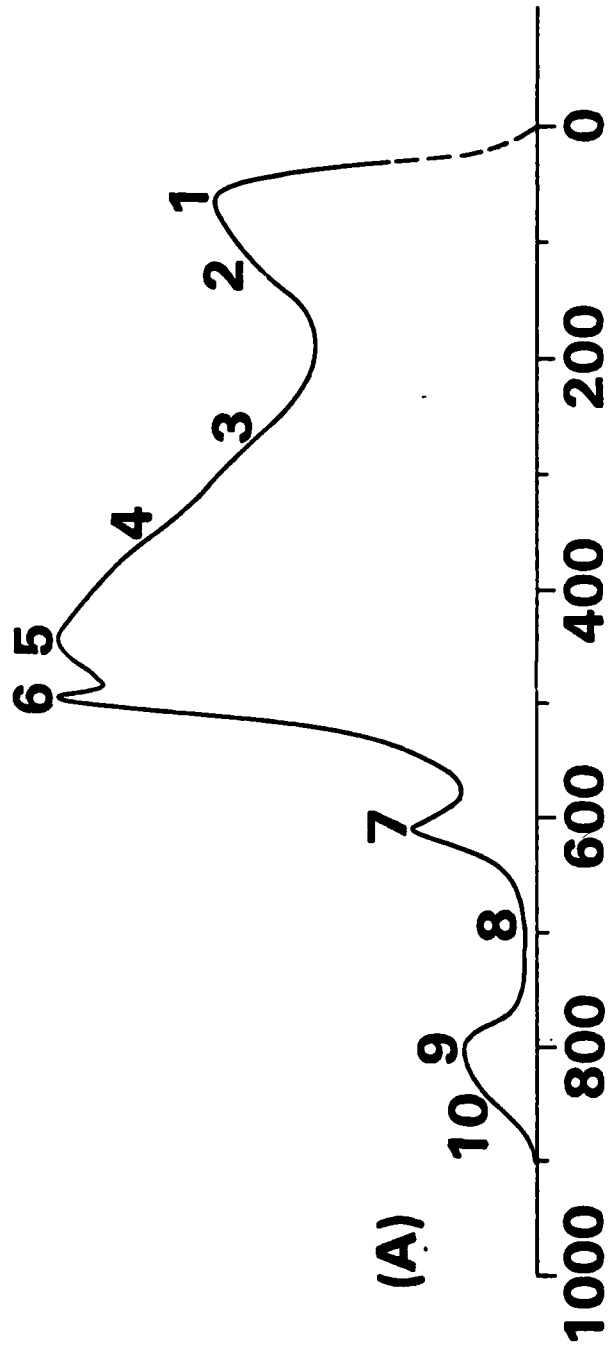
In Fig. 1 the Raman spectrum from a pure fused silica optical fiber is shown in the upper spectrum, (a). The Gaussian components used to model it are shown below in (c). Each Gaussian component correlates by number (1 to 10) to the corresponding feature in the Raman spectrum. The total integrated residual of the fit, using only Gaussian components corresponding to observed experimental features is negligible, 1%, as is the running residual shown graphically in (b) of Fig. 1.

From Fig. 1 it is evident that the component centered near  $235\text{ cm}^{-1}$  correlates with the weak shoulder near  $280\text{ cm}^{-1}$ . The  $280\text{ cm}^{-1}$  shoulder has been reported several times, e.g., Refs. (2,10,11). This feature corresponds to the infrared fundamental frequency which was invoked recently in explanations of the OH overtone structure.<sup>(1)</sup> The integrated intensity of the  $235\text{ cm}^{-1}$  component is 67 % of the integrated intensity of the most intense component at  $370\text{ cm}^{-1}$ , given a relative integrated intensity of 100 in Table I. The  $235\text{ cm}^{-1}$  component is thus the third most intense Raman component in the fused silica spectrum, which strongly supports the recent infrared combination assignments.<sup>(1)</sup> (It should

CAPTION

Fig. 1. Gaussian computer deconvolution of the Raman contour from fused silica. (a) Raman contour from Ref. (9) after transferral to horizontal baseline, (b) the running residual, sum of Gaussian components minus experimental Raman amplitude, and (c) the Gaussian components. Same amplitude scale for (a), (b), and (c).





$\Delta$  WAVENUMBER ( $\text{cm}^{-1}$ )

(4)

be noted that the  $280\text{ cm}^{-1}$  shoulder correlates with a Gaussian component whose center is shifted to  $235\text{ cm}^{-1}$ . However, the present correlation does not require that the observed and computed features have exactly the same frequency.)

In addition to the unexpected intensity of the  $235\text{ cm}^{-1}$  component, it is noteworthy that the intensities of two other components at  $105$  and  $370\text{ cm}^{-1}$ , which also correspond to Raman shoulders, are surprisingly large. Furthermore, the peak Raman intensity near  $430\text{ cm}^{-1}$  does not correspond to the strongest, but rather to the second strongest component at  $460\text{ cm}^{-1}$ , having a relative integrated intensity of 85, Table I.

We next extended the Gaussian computer analysis to Raman regions not shown in Fig. 1, namely, to  $2600\text{ cm}^{-1}$ .<sup>(12)</sup> As before we demanded a strict correlation between features observed, and Gaussian components employed. Again good results were obtained with negligible residuals. The results of the computer analysis are given in Table I.

The Raman bands listed in Table I below either  $1055$  or  $1180\text{ cm}^{-1}$  refer primarily to one-phonon or fundamental vibrations, and the multi-phonon overtone and combination region extends from either  $1180$  or  $1460\text{ cm}^{-1}$  to  $2600\text{ cm}^{-1}$ , or above.<sup>(12)</sup> (It is uncertain whether the  $1180\text{ cm}^{-1}$  band is a one- or two-phonon vibration.)

CAPTION

Table I. Parameters obtained from Gaussian computer deconvolution of the Raman spectrum from fused silica optical fiber. Most intense component given a value of 100, second column. Components above  $830\text{ cm}^{-1}$  from spectra of Refs. (9,10).

TABLE I

Component Position (cm <sup>-1</sup> )	Relative Integrated Intensity	Half width (cm <sup>-1</sup> )
55	20	55
105	50	110
235	67	185
370	100	175
460	85	140
495	8	25
610	10	45
685	5	155
795	5	55
830	6	60
900	1	--
1055	3	70
1180	3	100
1460	--	140
1605	--	140
2015	--	100
2150	--	150
2305	--	115
2405	--	160

The tails of the multi-phonon components at 2015, 2150, 2350, and 2405  $\text{cm}^{-1}$ , Table I, extend from about 1950 to 2600  $\text{cm}^{-1}$ . This spread covers the infrared absorption region in fused silica for which bands between 3.8 and 5.1  $\mu\text{m}$ <sup>(13)</sup> have been reported and assigned to two-, three-, and four-phonon combinations of silica fundamentals. In the region above 2.0  $\mu\text{m}$ , the transmission loss of doped silica fibers is known to increase by several orders of magnitude because of multi-phonon combinations involving silica fundamentals.<sup>(13-15)</sup> Hence, the present Gaussian analysis may be of use in understanding high loss mechanisms in optical fibers.

In summary, we have used a new approach in the analysis of the Raman spectrum of fused silica, namely, decomposition into a set of Gaussian components, each of which is related to a known feature of the vibrational spectrum. This decomposition yields the relative amplitudes and widths of the components. Some components which are weak in the infrared spectrum, and poorly resolved in the Raman spectrum, are shown to be major components in this analysis. This finding confirms the inference made previously<sup>(1)</sup> that these components contribute to combinations which are part of the OH overtone absorption spectrum of silica glass.

### ACKNOWLEDGEMENTS

The authors are grateful to Dr. Julian Stone for suggesting this work, and for numerous useful comments and revisions. This work was supported by contracts from the Office of Naval Research.

## REFERENCES

1. "Overtone Vibrations of OH Groups in Fused Silica Optical Fibers," J. Stone and G. E. Walrafen, J. Chem. Phys. XX, XXXX(1982).
2. W. Wadia and L. S. Balloomal, Phys. Chem. Glasses 9, 115(1968).
3. R. Shuker and R. W. Gammon, Phys. Rev. Lett. 25, 222(1970).
4. G. E. Walrafen and R. H. Stolen, Solid State Commun. 21, 417(1977).
5. G. E. Walrafen and S. R. Samanta, J. Chem. Phys. 68, 4672(1978).
6. C. M. Hartwig, J. Chem. Phys. 66, 227(1977).
7. G. E. Walrafen and S. R. Samanta, J. Chem. Phys. 69, 493(1978).
8. Because the polarization is scrambled in an optical fiber, the spectrum shown in Fig. 1 refers to the forward scattering condition  $Z\begin{pmatrix} x & x \\ y & y \end{pmatrix}Z$ .
9. G. E. Walrafen, P. N. Krishnan, and S. W. Freiman, J. Appl. Phys. 52, 2832(1981).
10. R. H. Stolen and G. E. Walrafen, J. Chem. Phys. 64, 2623(1976).
11. G. E. Walrafen and J. Stone, Appl. Spectrosc. 29, 337(1975).
12. G. E. Walrafen, Appl. Spectrosc. 29, 179(1975). See p. 183, Fig. 3.
13. T. Izawa, N. Shibata, and A. Takeda, Appl. Phys. Lett. 31, 33(1977).
14. H. Osanai, T. Shioda, T. Moriyama, S. Araki, M. Horiguchi, T. Izawa, and H. Takata, Elect. Lett. 12, 549(1976).
15. T. Miya, Y. Terunuma, T. Hosaka, and T. Miyashita, Elect. Lett. 15, 106(1978).

TECHNICAL REPORT DISTRIBUTION LIST, GEN

	<u>No.</u> <u>Copies</u>		<u>No.</u> <u>Copies</u>
Office of Naval Research Attn: Code 472 800 North Quincy Street Arlington, Virginia 22217	2	U.S. Army Research Office Attn: CRD-AA-IP P.O. Box 1211 Research Triangle Park, N.C. 27709	1
ONR Branch Office Attn: Dr. George Sandor 536 S. Clark Street Chicago, Illinois 60605	1	Naval Ocean Systems Center Attn: Mr. Joe McCartney San Diego, California 92152	1
ONR Area Office Attn: Scientific Dept. 715 Broadway New York, New York 10003	1	Naval Weapons Center Attn: Dr. A. B. Anster, Chemistry Division China Lake, California 93555	1
ONR Western Regional Office 1030 East Green Street Pasadena, California 91105	1	Naval Civil Engineering Laboratory Attn: Dr. R. W. Drisko Port Hueneme, California 93401	1
ONR Eastern/Central Regional Office Attn: Dr. L. H. Peebles Building 114, Section D 665 Summer Street Boston, Massachusetts 02210	1	Department of Physics & Chemistry Naval Postgraduate School Monterey, California 93940	1
Director, Naval Research Laboratory Attn: Code 6100 Washington, D.C. 20390	1	Dr. A. L. Slafkosky Scientific Advisor Commandant of the Marine Corps (Code RD-1) Washington, D.C. 20380	1
The Assistant Secretary of the Navy (REGS) Department of the Navy Room 4E736, Pentagon Washington, D.C. 20350	1	Office of Naval Research Attn: Dr. Richard S. Miller 800 N. Quincy Street Arlington, Virginia 22217	1
Commander, Naval Air Systems Command Attn: Code 310C (H. Rosenwasser) Department of the Navy Washington, D.C. 20360	1	Naval Ship Research and Development Center Attn: Dr. G. Bosnjian, Applied Chemistry Division Annapolis, Maryland 21401	1
Defense Technical Information Center Building 5, Cameron Station Alexandria, Virginia 22314	22	Naval Ocean Systems Center Attn: Dr. S. Yamamoto, Marine Sciences Division San Diego, California 91232	1
Dr. Fred Saalfeld Chemistry Division, Code 6100 Naval Research Laboratory Washington, D.C. 20375	1	Mr. John Boyle Materials Branch Naval Ship Engineering Center Philadelphia, Pennsylvania 19112	1



TECHNICAL REPORT DISTRIBUTION LIST, 051A

	<u>No. Copies</u>		<u>No. Copies</u>
Dr. M.A. El-Sayed Department of Chemistry University of California, Los Angeles Los Angeles, California 90024	1	Dr. M. Rauhut Chemical Research Division American Cyanamid Company Bound Brook, New Jersey 08905	1
Dr. E. R. Bernstein Department of Chemistry Colorado State University Fort Collins, Colorado 80521	1	Dr. J. I. Zink Department of Chemistry University of California, Los Angeles Los Angeles, California 90024	1
Dr. C. A. Heller Naval Weapons Center Code 6059 China Lake, California 93555	1	Dr. D. Haarer IBM San Jose Research Center 5600 Cottle Road San Jose, California 95143	1
Dr. J. R. McDonald Chemistry Division Naval Research Laboratory Code 6110 Washington, D.C. 20375	1	Dr. John Cooper Code 6130 Naval Research Laboratory Washington, D.C. 20375	1
Dr. G. B. Schuster Chemistry Department University of Illinois Urbana, Illinois 61801	1	<del>Dr. William M. Jackson Department of Chemistry Howard University Washington, DC 20059</del>	<del>1</del>
Dr. A. Adamson Department of Chemistry University of Southern California Los Angeles, California 90007	1	<del>Dr. George F. Walraffen Department of Chemistry Howard University Washington, DC 20059</del>	<del>1</del>
Dr. H. S. Wrighton Department of Chemistry Massachusetts Institute of Technology Cambridge, Massachusetts 02139	1		

	<u>No. Copies</u>
Dr. Rudolph J. Marcus Office of Naval Research Scientific Liaison Group American Embassy APO San Francisco 96503	1

Mr. James Kelley DTNSRDC Code 2803 Annapolis, Maryland 21402	1
--	---

FILMED

2-8