(NASA-CR-169309) PARAMETERS OF CO2 BANDS NEAR 3.6 MICRONS (Ohio State Univ., Columbus.) 21 p HC A02/MF A01 CSCL 07D

N82-32438

Unclas
G3/25 28897

Parameters of CO_2 Bands Near 3.6μm*

M. L. Hoke

J. H. Shaw

Department of Physics
The Ohio State University
Columbus Ohio 43210

---

*This work was supported in part by NASA Grant NSG-7469.

Abstract

The intensities, widths, and positions of lines of three CO_2 bands near 2750 cm^{-1} have been determined. The results are in general agreement with other measured and estimated values.

Introduction

A group of CO_2 bands near 2600cm^{-1} has recently been investigated by the nonlinear, least-squares method (NLLS) of whole-band analysis.[1,2] The spectra of a similar set of bands near 2750cm^{-1}, shown in Fig. 1, have also been analyzed by this technique. These spectra were obtained by coadding 750 interferograms collected by a Nicolet Fourier transform spectrometer. No apodization was applied to the composite interferograms before transformation. The SNR of the upper spectrum, Spectrum I, is about 600 and that of the lower spectrum, Spectrum II, is about 350. The spectral resolution of both is about 0.07cm^{-1}. Spectrum I was obtained with a path length of 476m through a naturally-occurring sample of CO_2 at a pressure of 177 torr and a temperature of 294K A path length of 994m at 741 torr and 292K was used to obtain Spectrum II.

The descriptions of the CO_2 bands in Table 1 were obtained from the work of Rothman and Young.[3] The strongest band in Table 1 is about ten times weaker than the corresponding band near 2614cm^{-1}. Thus, although reasonable values for the widths of the lines near 2600cm^{-1} have been obtained from previous analyses[1] of these bands in Spectrum I, accurate line widths could not be obtained from the upper spectrum in Fig. 1 although the positions of the lines could be well-determined. Estimates of the line widths were obtained from Spectrum II, although these lines are too wide to allow their positions to be determined as precisely as those in Spectrum I.

Lines of all three bands are present in these spectra. Information from aproximately 100 lines of band I, sixty lines of band II, and 40 lines of the subbands of band III, most of which are unresolved, contributed to the analysis.

Spectral Analysis

The method of analysis and the models used to describe the spectra are very similar to those used previously.[1,2]

The vibration-rotation, energy-level models and the expressions for the relative intensities of the CO_2 bands have been described by Rothman and Young.[3] We were able to determine band origins for all of the bands in Table 1. In addition, the quantities B", D", B' and D' were estimated for band I, and by fixing B" and D" to the values reported by Guelachvili,[4] estimates of B' and D' for the upper state of band II were obtained. However, only the sums B' + B" were obtained for the subbands of band III.

The term $(1+\xi m)^2$ was used to describe the influence of vibration-rotation interactions on CO_2 line intensities. The value of ξ obtained for the strongest band was less than the standard deviation of 10^{-3}; no attempt was made to estimate ξ for the other bands.

The profiles of the lines were found to be adequately described by the Lorentz shape and the $|m|$-dependence of the widths was described by the expression of Winters et al.[5]

$$\alpha|m| = W_1 + W_2 \exp[-W_3 |m|] + W_4|m| \exp[-B''|m|(|m|-1)/kT]. \quad (1)$$

This expression, which has four adjustable parameters, described the $|m|$ dependence of the CO_2 lines near 2600cm^{-1} satisfactorily.(1)

The influence of instrumental effects due to the finite optical-path-difference, the finite source size, and due to residual phase error[6,7] on the spectra were included by using the models described by Hoke.[8] In those cases where they could be compared, the parameter values in these models agreed with those obtained from other analyses.[1,2,8]

The influence of continuous absorption by the wings of distant CO_2 bands

ORIGINAL PAGE IS OF POOR QUALITY

Table 1. The band origins, identifications, and intensities of CO_2 bands between 2700 and 2800cm^{-1} from the tabulation of Rothman and Young (Ref. 3).

Band	Band Center (cm^{-1})	Molecule	Transition	Band Intensity[a] (10^{24} cm^{-1}/mol cm^{-2})
I	2757.229	628	20001-00001	2.20
II	2776.000	627	20001-00001	0.23
III	2791.616	628	21101-01101	0.15

[a] These band intensities were obtained by assuming the isotopic abundances in naturally-occurring CO_2.

Rotational Constants

Four sets of rotational constants for band I are given in Table 2, together with experimental values obtained by Guelachvili,[4] and Hoke and Shaw,[2] and values estimated by Chedin[9] and Rothman and Young.[3] The experimental values[2,4] were obtained from other band systems. The ranges of values reported by Hoke and Shaw[2] are caused by correlations among the rotational constants and other retrieved parameters and also by the non-uniqueness of NLLS solutions.

Two sets of constants are reported from each spectrum. In one case, the B" and D" values were retrieved from the spectra and, in the other case, these were fixed to the values of Guelachvili.[4] As in the previous analysis of the corresponding band at 2614cm^{-1}, it was found that the retrieved values of B" were consistently smaller than that reported by Guelachvili[4] and that the SDR obtained with B" fixed was always smaller than that obtained by retrieving B".

The standard deviations in Table 2 were obtained from the analysis and, as noted previously,[2] they are often optimistically small. The estimated correlation coefficients between the retrieved parameters are also obtained. These show variations from retrieval to retrieval but the correlations between the parameters in Table 2 agree, in both their relative values and absolute magnitudes, with those which would be obtained by performing a linear, least-squares analysis of the line positions.[10]

The largest SDR value was obtained for retrieval A in Table 2. The differences in the line positions calculated from these parameters and the other sets of parameters are shown in Fig. 3. For $|m| < 50$, all the line positions obtained from the retrieved parameter sets are consistent to ± 0.003cm^{-1}. Although the line positions obtained from the spectrum of the higher pressure sample are less precise than those obtained from spectrum I the results confirm the conclusions of Freed et al[11] and of Hollins and Jordan[12] that the pressure shifts of infrared

CO_2 lines are small compared with their widths.

The lines of the $^{16}O^{12}C^{17}O$ band are much weaker than those of band I and the upper state constants B' and D', given in Table 3, were obtained by fixing B" and D". These sets of constants give positions of lines with $|m| < 35$ which agree within $\pm$ 0.005cm^{-1}. This is less than one tenth of the observed line width.

Information about the weakest of the bands was only obtained from spectrum II. Initial estimates of the rotational constants were obtained by calculating the spectrum of bands I and II only and subtracting this from the observed spectrum. Many of the lines of band III, including the Q branch could then be seen. Since the lines of the two subbands were only resolved for $|m| > 15$ it was not possible to obtain satisfactory individual B' and B" values in the subsequent NLLS analysis.

Absolute values for the band origins were obtained by calibrating the spectra against the previously-measured positions[13,14] of water vapor lines present in the spectra. The estimated accuracy of the band origins[15], $\pm 2 \times 10^{-3}$cm^{-1}, is smaller than the precision, about 10^{-4} cm^{-1}, estimated by the NLLS analyses. These band origins are compared with those of Rothman and Young[3] and Chedin[9] in Table 4.

Line Widths

It was assumed that the corresponding lines in each of the bands had the same width and all the widths were reduced to standard conditions of 296K, 760 torr by the relation

$$\alpha(|m|, P,T) = \alpha(|m|, P_oT_o)\ (P/P_o)\ (T_o/T)^{1/2}. \qquad (2)$$

The widths obtained from spectrum II are compared with those obtained from the previous analyses of the bands near 2600cm^{-1} in Fig. 4. In both cases the dominant band is due to $^{16}O^{12}C^{18}O$ and the broadening is due to the isotope $^{12}C^{16}O_2$. The precision of each set of results in estimated to be about 2-3%.

Since the maximum difference between the two sets of widths is less than 4% the effects due to differences in the vibrational transitions involved are small. The values of the constants W_i in Eq. (1), which are given in Table 5, are those which produced the curves in Fig. 4. They were obtained from the solutions with the largest SDRs. Other sets of values of W_i, obtained from retrievals with almost equally good fits to the experimental data, gave curves almost identical to that shown in Fig. 5, even though the values of the constants differed by several times the standard deviations given in Table 5. This behavior is consistent with that found for most of the other parameter values.[1,2]

Intensities

The band sums, the sums of the intensities of all the lines in each band, were calculated as described previously.[1] The values in Table 6 were obtained from the analysis with the largest SDR. The spreads obtained from almost equally good retrievals are also given together with the values estimated by Rothman and Young.[3] These spreads are an order of magnitude larger than the standard deviations obtained by the NLLS analyses. The results for bands II and III were obtained only from spectrum II and, in order to obtain band sum III, it was necessary to fix the sums B' + B". The experimental intensities for two of the bands are significantly larger than those estimated by Rotham and Young.[3]

Conclusions

The values for the band sum, the line widths, and the rotational parameters of band I have been obtained with accuracies sufficient for use in most atmospheric transmittance calculations. The corresponding values for bands II and III describe the experimental data available adequately. The results are in satisfactory agreement with the previous measurements of Guelachavili[4] and Hoke and Shaw[1,2,8] and with the estimates of Rothman and Young.[3]

References

1. M. L. Hoke and J. H. Shaw, "Analysis of CO_2 bands near $2600cm^{-1}$," Appl. Opt., 21, 929 (1982).
2. M. L. Hoke and J. H. Shaw, "Rotational analysis of CO_2 bands near 4μm," Appl. Opt., 21, 935 (1982).
3. L. S. Rothman and L. D. S. Young, "Infrared energy levels and intensities of carbon dioxide-II," Jour. Quant. Spectrosc. Radiat. Transfer, 25, 505 (1981).
4. G. Guelachvili, "High resolution Fourier spectra of carbon dioxide and three of its isotopic species near 4.3μm," J. Mol. Spec., 79, 72 (1980).
5. B. H. Winters, S. Silverman, and W. S. Benedict, "Line shape in the wing beyond the band head of the 4.3μ band of CO_2," Jour. Quant. Spectrosc. Radiat. Transfer, 4, 527 (1964).
6. G. A. Vanasse and H. Sakai, "Fourier Spectroscopy" in "Progress in Optics, Vol. VI," E. Wolf ed., North-Holland, Amsterdam (1967).
7. C. R. Anderson and D. R. Mattson, "Phase correction techniques in Fourier transform-infrared (FT-IR)," Soc. Photo-Opt. Instru. Eng. 289, 199 (1981).
8. M. L. Hoke "Analysis of CO_2 bands near $2600cm^{-1}$, Ph.D diss. Ohio State Univ. (1982).
9. A. Chedin, "The carbon dioxide molecule," J. Mol. Spec., 76, 430 (1979).
10. D. L. Albritton, A. L. Schmeltekopf and R. N. Zare, "An introduction to the least-squares fitting of spectroscopic data" in "Modern Spectroscopy. Modern Research II," K. Narahari Rao, ed., Academic Press New York (1966).
11. C. Freed and R. G. O'Donnell, "Advances in CO_2 laser stabilization using the 4.3μm fluorescence technique" Metrologia, 13, 151 (1977).
12. R. C. Hollins and D. L. Jordan, "Pressure shift in an atmospheric pressure CO_2, N_2, He gas mixture," J. Phys. B. 15, L 491 (1982).

13. L. A. Pugh, Ph.D dissertation, "A detailed study of the near infrared spectrum of water vapor," Ohio State University (1972).

14. C. Camy-Peyret and J. M. Flaud, "Line positions and intensities in the ν_2 band of $H_2{}^{16}O$," Mol. Phys., 32, 523 (1976).

15. R. L. Hawkins, M. L. Hoke, and J. H. Shaw "Wavenumber calibration of Fourier transform spectra," Appl. Spectrosc. (accepted).

Table 1. The band origins, identifications, and intensities of CO_2 bands between 2700 and 2800cm^{-1} from the tabulation of Rothman and Young (Ref. 3).

Band	Band Center (cm^{-1})	Molecule	Transition	Band Intensity[a] (10^{24} cm^{-1}/mol cm^{-2})
I	2757.229	628	20001-00001	2.20
II	2776.000	627	20001-00001	0.23
III	2791.616	628	21101-01101	0.15

[a] These band intensities were obtained by assuming the isotopic abundances in naturally-occurring CO_2.

Table 2. Rotational constants for Band I (20001-00001,626) obtained in this work and in other studies.

Retrieval	Spectrum	SDR	B'' (cm^{-1})	B' (cm^{-1})	10^8 D'' (cm^{-1})	10^8 D' (cm^{-1})
A	I	400	0.36818277(56)	0.36903714(22)	12.130(37)	8.882(36)
B	I	392	0.36818571[a]	0.369036189(46)	11.9030[a]	8.494(96)
C	II	170	0.3681616(75)	0.3690155(76)	11.75(35)	8.416(35)
D	II	168	0.36818571[a]	0.36903951(87)	11.9030[a]	8.550(52)
			0.36818571(52)[a]		11.9030(186)[a]	
			0.3681771[b]	0.369039[b]	11.7[b]	7.7[b]
			0.368186[c]	0.369024[c]	11.9[c]	8.8[c]
			0.36816235(22)[d]		11.5660(49)[d]	
			0.36818571[a,d]		12.413(18)[d]	

[a] Guelachivili (Ref. 4)

[b] Rothman and Young (Ref. 3)

[c] Chedin (Ref. 9)

[d] Range of values obtained by Hoke and Shaw (Ref. 2)

ORIGINAL PAGE IS
OF POOR QUALITY

Table 3. Upper State Rotational Constants for Band II (20001-0001,627).

Source	B' (cm^{-1})	10^8 D' (cm^{-1})
Retrieval B[†]	0.379172(7)	0.0[*]
Retrieval D[†]	0.379327(17)	16.15(12)
Rothman[a]	0.379270	8.8
Chedin[b]	0.379248	9.3

[†] see Table 2 for details

[*] standard deviation not obtained

[a] (Ref. 3)

[b] (Ref. 9)

Table 4. Origins of CO_2 bands between 2700 and 2800 cm^{-1}

Band (see Table 2)	Molecule	Rothman and Young (cm^{-1})	Chedin[**] (cm^{-1})	This Work (cm^{-1})
I	628	2757.229	2757.211	2757.183(2)
II	627	2776.000	2775.610	2775.595(2)
III	628	2791.616	2791.593	2791.512(2)

[*] Ref. 3

[**] Ref. 10

Table 5. Best estimates of the parameters of the Winters et al (Ref. 5) model for describing the dependence of CO_2 line widths on $|m|$.

Parameter**	Previous work*	This work
W_1 (cm^{-1}/atm)	$8.34(2)\times10^{-2}$	$8.0732(8)\times10^{-2}$
W_2 (cm^{-1}/atm)	$5.83(6)\times10^{-2}$	$6.15(4)\times10^{-2}$
W_3	-0.1539(4)	-0.179(9)
W_4 (cm^{-1}/atm)	$1.82(2)\times10^{-3}$	$1.89(9)\times10^{-3}$

*See Reference 1.

**Corrected to 296 K, 760 torr.

Table 6. Band Intensities.

Band	Molecule	Intensity (10^{24} cm^{-1}/mol cm^{-2})		
		Rothman and Young[a]	Spectrum I*	Spectrum II*
I	628	2.20	3.31 (12)	3.28 (12)
II	627	0.23	-	0.214 (12)
III	628	0.15	-	0.255(15)

*The values in brackets represent the total scatter in the estimated values.

[a] See Ref. 3.

Fig. 1. Top: Spectrum of a 476m path of CO_2, pressure 177 torr, temperature 294K; bottom: spectrum of a 994m path of CO_2, pressure 741 torr, temperature 292K. These are referred to as Spectrum I and Spectrum II, respectively, in the text.

Fig. 2. Upper left: a portion of Spectrum II in a region where there is little line absorption. Upper right. a portion of the same spectrum. Bottom: the difference between the observed and calculated values, shown on an expanded scale.

Fig. 3. The differences in the line positions calculated from the constants in retrieval A, Table 3 and the positions calculated from the other retrievals (labeled according to the retrieval identification in Table 3), including those calculated from the constants of Rothman and Young (R) and Chedin (Ch).

Fig. 4. The |m| dependence of the widths of $^{16}O^{12}C^{18}O$ lines broadened by $^{12}C^{16}O_2$ (reduced to 296K, 760 torr). The top curve was obtained from the analysis of the 20002-0001 band at 2614 cm^{-1} (see reference 1). The bottom curve was obtained from the analysis of the 20001-00001 band at 2757 cm^{-1}.

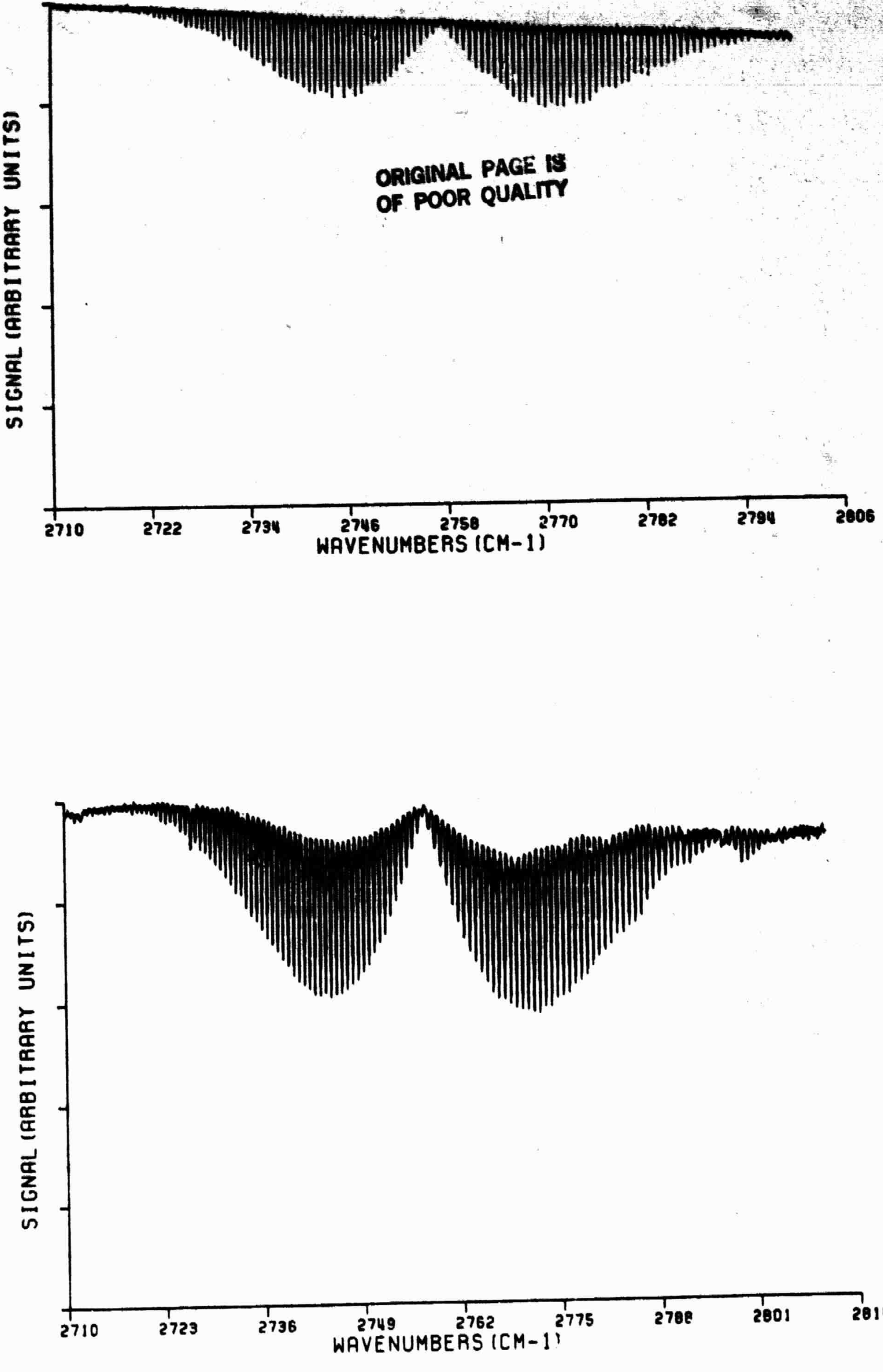
SIGNAL (ARBITRARY UNITS)
2710
2722
2734
2746
2758
2770
2782
2794
2806
WAVENUMBERS (CM-1)
SIGNAL (ARBITRARY UNITS)
2710
2723
2736
2749
2762
2775
2788
2801
2814
WAVENUMBERS (CM-1)

Fig. 1.

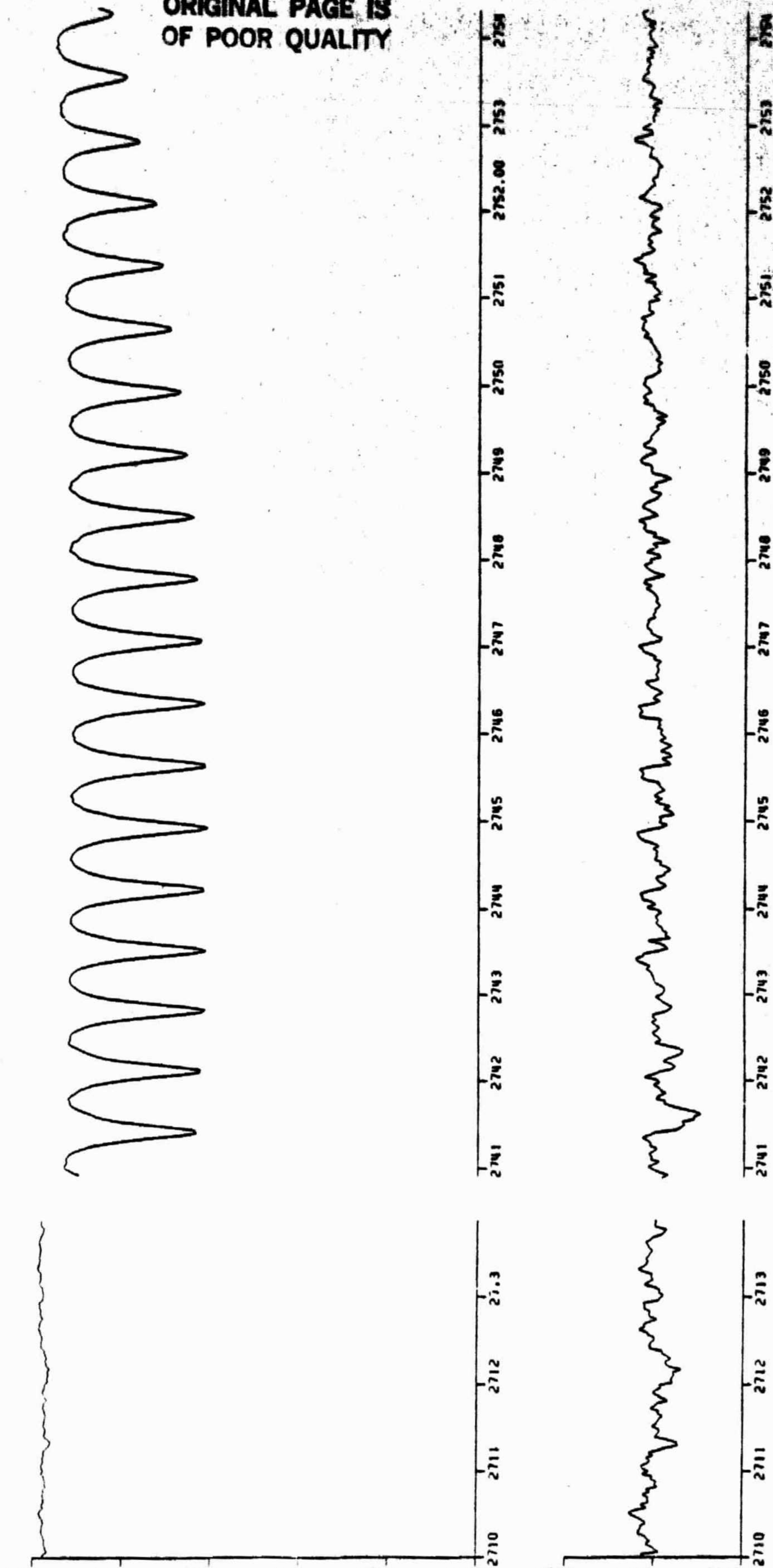
SIGNAL (ARBITRARY UNITS)
0.00
0.20
0.40
0.60
0.80
1.00
RESIDUAL
-0.05
0.00
0.05
2710
2711
2712
2713
2741
2742
2743
2744
2745
2746
2747
2748
2749
2750
2751
2752
2752.00
2753
2754

Fig. 2

ORIGINAL PAGE IS
OF POOR QUALITY

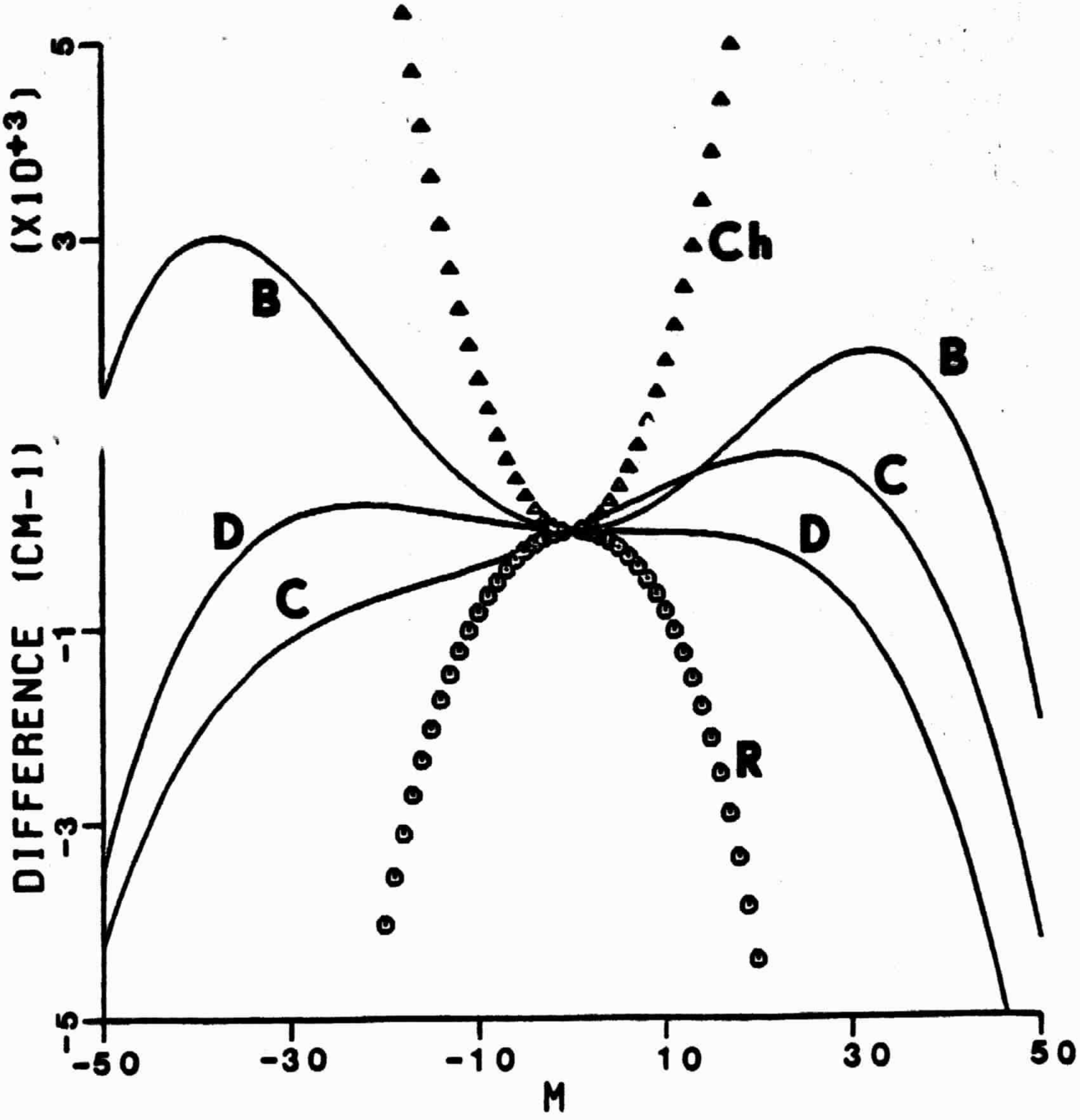

Fig 3

ORIGINAL PAGE IS
OF POOR QUALITY

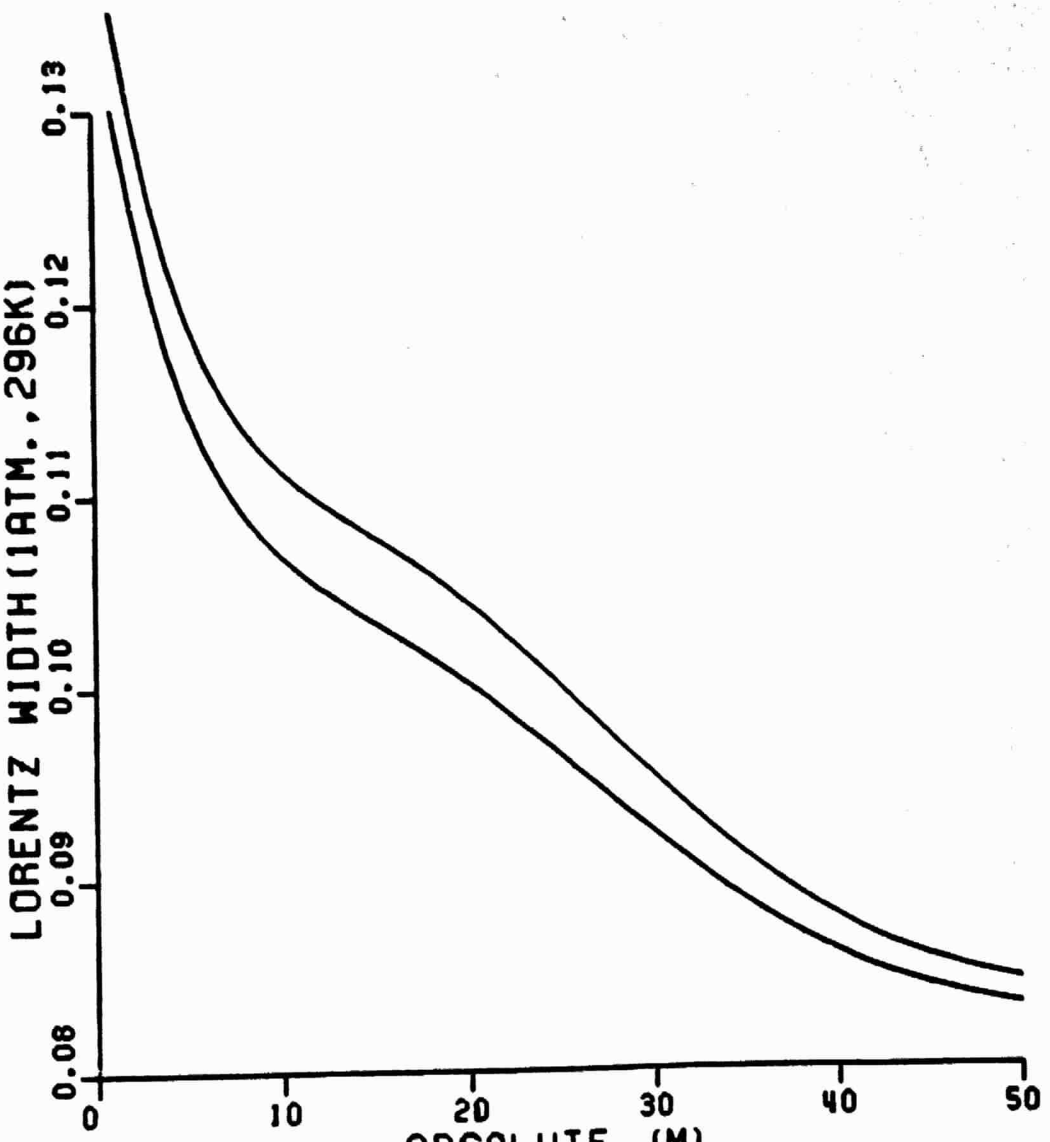

Fig. 4