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Nitrogen-, Oxygen-, and Air-Broadened Widths and Relative Intensities of N_2O Lines near 2450 cm^{-1}*

R. L. Hawkins

J. H. Shaw

Department of Physics,
The Ohio State University,
Columbus, Ohio 43210

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Abstract

Spectra of the $\nu_1+2\nu_2$ and the weak underlying $\nu_1+3\nu_2-\nu_2$ band of N_2O near 2450 cm^{-1} have been analyzed by the nonlinear, least-squares, whole-band technique. The oxygen-, nitrogen-, and air-broadened line widths and the relative line intensities were determined. The air-broadened widths, for $|m|>3$, are in agreement with those in the 1980 AFGL line listing and the relative band intensities also agree, within about 20%, with the values in this listing.

Introduction

There are substantial differences between the few measurements of the oxygen-or air-broadened widths [1] of N_2O lines and the corresponding calculated line widths.[2] Although more measurements of N_2-broadened widths are available these also vary considerably (see, e.g. references 3-10).

The measurement of pressure-broadened N_2O line widths is difficult because the spacing of the lines, about 0.8 cm^{-1}, is less than five times the full widths of the lines at atmospheric pressure. The problem is compounded because N_2O bands occur in groups consisting of a strong band and weaker underlying bands.

Many of these analytical difficulties can be reduced by the nonlinear least-squares, whole-band method of analysis.[11-13] This method has been used to measure the N_2-, O_2-, and air-broadened widths of lines up to $|m|=40$ in the $\nu_1+2\nu_2$ band of N_2O near 2450 cm^{-1} in spectra obtained with a Fourier transform spectrometer. The relative intensities of the lines in this band and the weaker, underlying $\nu_1+3\nu_2-\nu_2$ have also been determined.

Models

The method requires models for all the factors which influence the observed spectrum. In this analysis the line shapes, positions, widths, and relative intensities, and instrumental effects [14] such as channel spectra and other background variations, the effects of finite optical retardation, and beam divergence due to the finite aperture size, were modelled. The phase correction of the observed spectrum was also retrieved as part of the least-squares fit.

The line positions $\nu_0(m)$ and the lower state energies $E''(m)$ were obtained from the molecular constants of Amiot and Guelachvili.[15] These line positions were used to determine the frequency calibration of our spectra.

The lines were assumed to have a Lorentz shape and the $|m|$-dependence of the widths was modelled by the empirical relation

$$\alpha(|m|,\ P_o,\ T_o) = a\ \exp\ [\ -\ b|m|] + \sum_{i=0}^{9} c_i\ T_i(x), \tag{1}$$

where the standard pressure P_o is one atmosphere, T_o is 296 K, and $T_i(x)$ is the ith Tchebyschev polynomial. Since the absorption by lines with $|m|>50$ was insignificant, the argument x was reduced to the range [-1,1], on which the $T_i(x)$ are defined, by setting $x = (|m|-25)/25$. The coefficients c_i for $i > 9$ were not determined since they were found to be much smaller than those for $i \leq 9$. The exponential term was included to model rapid changes in the line widths for $1 \leq |m| \leq 3$. The same expression and values for the coefficients were used to describe the lines of both N_2O bands.

The line widths in the N_2O samples were obtained from Eq. (1) and the relations[16]

$$\alpha_n\ (|m|,P,T) = \alpha\ (|m|,P_o,T_o)\ \ (P/P_o)\ \ (T/T_o)^{\frac{1}{2}}, \tag{2}$$

$$\alpha_{tot}\ (|m|,P,T) = \sum_n (P_n/P)\alpha_n\ \ (|m|,\ P,T), \tag{3}$$

and

$$P = \sum_n P_n, \tag{4}$$

where P_n is the partial pressure of the nth gas in the sample and $\alpha_n\ (|m|,T,P)$ is the fractional width due to the nth gas. The contributions of self-broadening were less than 2% in the spectra analyzed and these contributions were included by using the self-broadened widths reported by Toth.[5]

Line intensities were modelled[17] by

$$S_o(m) = W\ (1 + Cm + Dm^2)\ \nu_o(m)\ [Q(T_o)/Q(T)]\ [(m^2-\ell^2)/|m|]\ \exp\ [-hcE''(m)/kT], \tag{5}$$

where the vibrational partition function Q(T) has been tabulated for N_2O by Gray Young,[18] and the vibrational angular momentum quantum number ℓ is zero for the $\nu_1+2\nu_2$ band and unity for the $\nu_1+3\nu_2-\nu_2$ band. It is assumed that the square of the dipole moment matrix element can be written as

$$|R(m)|^2 = |R(0)|^2 \, (1 + Cm + Dm^2), \qquad (6)$$

and that W, in Eq(5), is proportional to the square of the rotationless matrix element

$$W = |R(0)|^2 \, 8\pi^3/3hc \; Q(T_o). \qquad (7)$$

The constants C and D could only be obtained for the stronger $\nu_1 + 2\nu_2$ band.

Experimental Conditions

The data were collected with a Nicolet Fourier Transform Spectrometer and an InSb detector. Signal - to - noise ratios (SNR) in excess of 300 were obtained by coadding 250 or more interferograms collected over periods of one to four hours. The spectral resolution was about 0.07 cm^{-1}. Usually 2821 data points between 2415 and 2500 cm^{-1} were analyzed in each retrieval.

A summary of the experimental conditions is given in Table 1. Sample A was contained in a 10m multiple traversal cell and the N_2O pressure was less than one torr. A 40 cm absorption cell was used for the other samples, with N_2O partial pressures of about 14 torr and total pressures near one atmosphere. There was evidence that changes in the partial pressures of N_2O occurred when the broadening gases were added. These changes were attributed to adsorption/desorption effects on the cell walls and they prevented absolute line intensities from being obtained.

The temperature of the cell containing sample A was monitored by calibrated thermocouples and a mercury-in-glass thermometer was used to measure the temperatures of the other samples. With the exception of sample D, the temperatures did not change by more than a few tenths of a kelvin during the data collection.

A temperature change of about 3K occurred as the interferograms of sample D were collected. The temperature of this sample in Table 1, which was used in the analysis, is a mean temperature. It was estimated, from Eq.(2), that the change in the line widths due to this temperature variation was less than 0.5%. Because of the Boltzmann factor in Eq.(5) there was a significantly larger change in the intensities of the lines with high |m| values, and in the relative intensities of the $(\nu_1+3\nu_2-\nu_2)$ lines which arise from the ν_2 vibrational state.

Results

The principle criteria for evaluating the results of least-squares analyses are the comparison of the rms difference between the observed and calculated spectra to the rms noise in the data and the lack of systematic patterns in the spectrum of the residuals.

A portion of the best-fit, calculated spectrum is compared to the observed spectrum of sample D in Figure 1. The residuals spectrum is also shown. The rms residual difference is less than 0.2% and the rms noise is about 0.1% of the maximum signal. Similar differences of about 0.1% were found between the rms difference and rms noise for the other spectra and these fits were considered satisfactory. The program for calculating spectra was designed to give accuracies of a few tenths per cent and thus these fits are at the limit of the computational methods. There was little evidence of systematic patterns in the spectra of the residuals.

A. Line Widths

The retrieved line widths $\alpha(|m|,P_0,T_0)$ are listed in Table 2 and plotted as functions of |m| in Fig. 2. The analytical program provides estimates of the standard deviations of the retrieved values of the parameters such as those in Eq.(1) and also the correlations between all the parameters estimated. However, it is difficult to obtain the standard deviations of quantities derived from these expressions such as the individual line positions, intensities and widths. Thus it is necessary to use other methods to estimate the precision

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of the results.

The experience gained during these analyses indicated that the line widths of samples B, C, and D could be consistently retrieved to about 3% and a somewhat lesser precision was found for the narrower lines of the lower pressure sample A, although the widths from both samples A and B agree within this estimated precision.

Equation (2) does not contain any a priori information about the shapes of the curves in Figure 2. For example, the curve is not constrained to be monotonically decreasing. Thus the similarity of the retrieved curves in Fig. 2, the agreement with the air-broadened line widths tabulated by Rothman,[19] and with the N_2-broadened widths recently reported by Toth,[7] all confirm the consistency of the results and suggest that the structures of the curves are real.

Although the retrieved O_2-broadened line widths are nearly twice as large as those calculated by Tejwani [2] this result is similar to the differences between the calculated [20] and observed [21] widths of O_2-broadened CO lines.

The retrieved air broadened widths are compared with those calculated from the independently measured N_2-and O_2-broadened widths in Table 1 by the expression

$$\alpha_{air}\ (\mathrm{calc}) = 0.79\alpha_{N_2} + 0.21\alpha_{O_2}, \qquad (8)$$

in Fig. 3. The largest difference, about 2.5%, is within the precision of the measurements. In analyzing the N_2O spectra in this region no evidence of deviations from the Lorentz shape was found.

B. Relative Line Intensities

The retrieved values of the ratio

$$R = W(\nu_1+3\nu_2-\nu_2)/W(\nu_1+3\nu_2), \qquad (9)$$

and the values of C and D in Eq. (5) are given in Table 1 for each of the spectra analyzed. Hoke and Shaw [12,13] have found that the standard deviations, estimated by the regression program and given in Table 1 are qualitatively useful but are also usually too small. A more objective estimate is obtained by finding the mean and standard deviation from several independent measurements. From these values, shown in the last row of Table 1, it is found that the ratio R has been determined to about 5%, the value of C is not significantly different from zero, and that D has been estimated to about 1%. The results obtained from sample D were not used to determine these means because of the temperature change which occurred during the collection of the interferograms. The intensities of the lines of the $\nu_1+3\nu_2-\nu_2$ band are less than 10% of the corresponding lines of the $\nu_1+2\nu_2$ band, and, because of the high sample pressures, they are all strongly overlapped by lines of the $\nu_1+2\nu_2$ band. Thus, much of the uncertainty in the value of R is attributed to the difficulty of estimating the intensities of the lines of the weaker band.

The band sum, the sum of the intensities of all the lines in a band, can be calculated from the values of W, C, and D. By using the parameter values in Table 1 the ratio of the band sums of the $\nu_1+3\nu_2-\nu_2$ and $\nu_1+2\nu_2$ bands is 0.138(7). The corresponding band sum ratio, based on the data given by Rothman [19] is 0.170.

The low values and large standard deviation of D retrieved from the O_2-broadened spectrum is attributed to the temperature change discussed earlier. It is interesting to note that, for $|m| = 40$, the effect of the mean value of D in Table 1 is to increase the line intensities of the $\nu_1+2\nu_2$ band by about 10% over the values expected if D were zero. A temperature change of 3K changes the same line intensities by about 5%. Thus accurate temperature control is essential for these types of measurements.

There appears to be no significant differences between the values of the constants in Table 1. Thus the line intensity parameters are not strongly dependent on the broadening gas. The peak absorptances of the strongest lines in sample A were about 65%, and about 40% in the other samples. Thus the ability to retrieve the line intensity parameters is not strongly affected by the peak absorptance of the lines.

Discussion

The internal agreement of the retrieved N_2O line widths and the agreement of the N_2-broadened widths with other recent measurements[8] indicate that these widths are probably accurate to about 3%.

The rotational dependence of $|R(m)|^2$ is sometimes written as $(1+\beta m)^2$ rather than $(1+Cm+Dm^2)$. These expressions are equivalent provided $C=2\beta$ and $D=\beta^2$. The retrieved values of C and D are not consistent with this alternative formulation.

Hoke and Shaw[12,13] have analyzed bands of CO_2 in the same spectral region in spectra obtained with the same instrument. The quality of both sets of results is similar and confirms the usefulness of this method of analysis.

Acknowledgments

We are pleased to acknowledge the assistance of John Devitt and Professor E.K. Damon in the collection of the spectra and the useful discussions with Dr. M. L. Hoke concerning the analyses. The extensive computations were performed with the facilities of the Instruction and Research Computer Center at the Ohio State University.

TABLE 1. Summary of the sample conditions, the best retrieved values of the ratio $W(\nu_1 + 3\nu_2 - \nu_2)/W(\nu_1 + 2\nu_2)$, and of the parameters C and D. The numbers in parentheses are the estimated standard deviations in units of the last digit quoted.

SAMPLE	Broadening gas	Total Pressure (torr)	Temp. (K)	rms residual (%)	$\frac{W(\nu_1 + 3\nu_2 - \nu_2)}{W\,\nu_1 + 2\nu_2}$	10^4C	10^4D
A.	N_2	550	296.6	0.40	1.33(1)	1.67(29)	0.643(7)
B.	N_2	744	296.1	0.27	1.25(1)	−0.80(43)	0.651(6)
C.	Air	748	292.6	0.29	1.23*(–)	2.84*(–)	0.640*(–)
D.	O_2	741	295.0**	0.19	1.25(1)	0.52(29)	0.551(31)
Mean [a]					1.27(5)	−0.66(226)	0.645(6)

* standard deviation not retrieved

** mean temperature

[a] excluding Sample D.

TABLE 2. Retrieved widths (cm^{-1}/atmosphere, 296 K) of N_2O lines broadened by N_2, O_2 and air.

|m|	N_2	O_2	AIR
1	0.1105	0.0972	0.1086
2	0.1023	0.0925	0.0992
3	0.0981	0.0898	0.0944
4	0.0961	0.0882	0.0921
5	0.0952	0.0872	0.0912
6	0.0948	0.0864	0.0907
7	0.0943	0.0857	0.0903
8	0.0937	0.0848	0.0897
9	0.0929	0.0839	0.0889
10	0.0919	0.0829	0.0880
11	0.0909	0.0819	0.0870
12	0.0898	0.0809	0.0860
13	0.0888	0.0799	0.0851
14	0.0878	0.0790	0.0843
15	0.0870	0.0782	0.0836
16	0.0863	0.0775	0.0830
17	0.0856	0.0768	0.0826
18	0.0851	0.0762	0.0822
19	0.0845	0.0756	0.0818
20	0.0840	0.0750	0.0814
21	0.0835	0.0744	0.0811
22	0.0829	0.0738	0.0806
23	0.0824	0.0732	0.0802
24	0.0818	0.0727	0.0797
25	0.0812	0.0721	0.0793
26	0.0807	0.0716	0.0788
27	0.0802	0.0711	0.0784
28	0.0798	0.0707	0.0780
29	0.0795	0.0704	0.0778
30	0.0792	0.0701	0.0776
31	0.0791	0.0700	0.0776
32	0.0791	0.0699	0.0776
33	0.0791	0.0699	0.0776
34	0.0791	0.0699	0.0777
35	0.0790	0.0700	0.0777
36	0.0790	0.0700	0.0777
37	0.0788	0.0700	0.0776
38	0.0785	0.0700	0.0774
39	0.0781	0.0699	0.0772
40	0.0777	0.0698	0.0770

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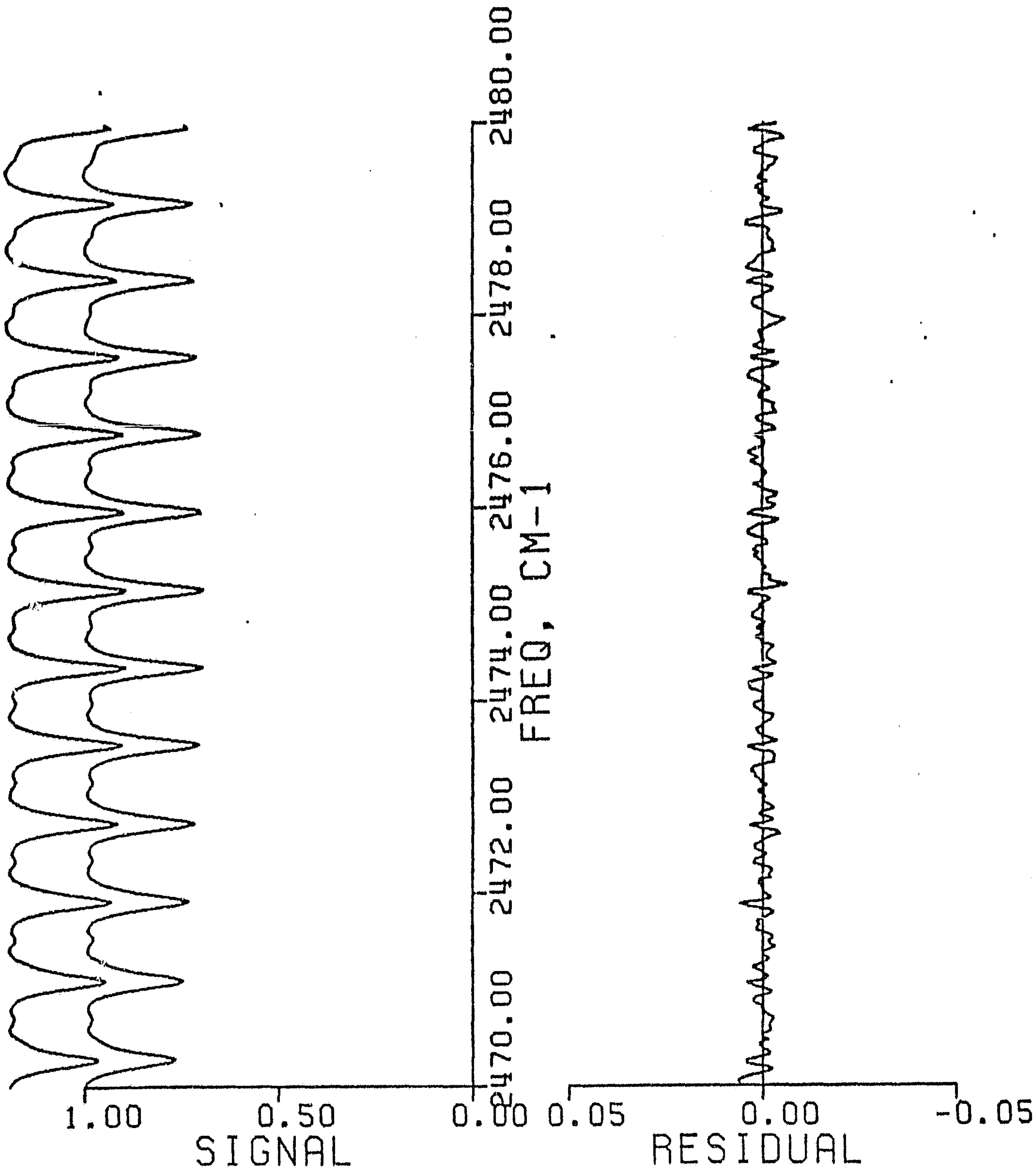
Figure Captions

Fig. 1. (top) A portion of the experimental O_2-broadened spectrum (sample D in Table 1), the best-fit, calculated spectrum, raised by about 20% is also shown; (bottom) the residual differences between the calculated and the observed spectrum with the vertical scale expanded by a factor of ten. The feature at 2457 cm^{-1} is the unmodelled Q-branch of the $\nu_1 + 3\nu_2 - \nu_2$ band. In the analysis, the data between 2457.2 and 2457.8 cm^{-1} were assigned a weight of zero.

Fig. 2. Retrieved line widths (cm^{-1}/atm, 296 K). Top curve (squares): N_2-broadened widths, middle curve (circles): air-broadened widths, bottom curve (triangles): O_2-broadened widths. The air-broadened widths in the 1980 AFGL line listing (see reference 19) are shown by the symbol (+) and the N_2- and O_2- broadened widths of the $J=5\rightarrow6$ pure rotational line of N_2O measured by French and Arnold (reference 1) are designated FA.

Fig. 3. The experimentally determined dependence of the air-broadened line widths on $|m|$ (squares) is compared with that calculated from the measured N_2-and O_2-broadened line widths.

Fig-1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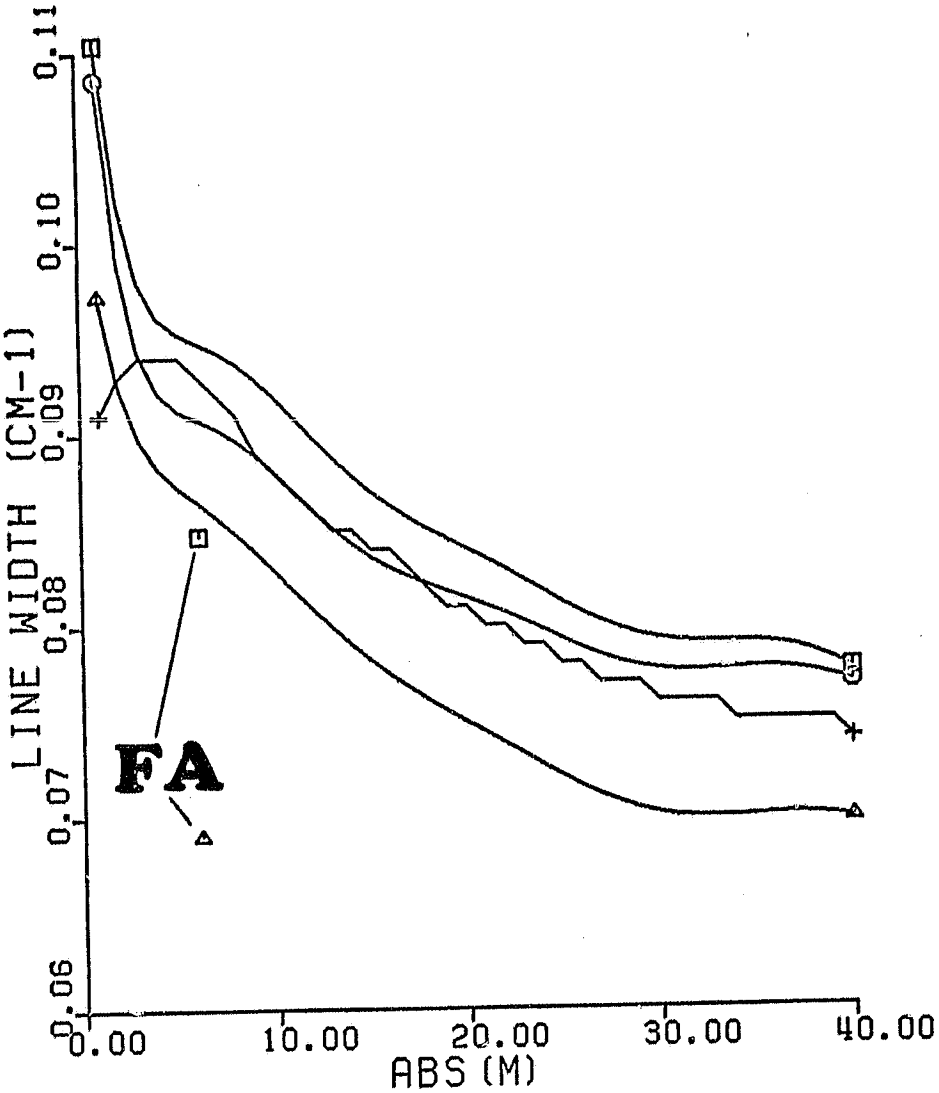
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Fig 2