

LETTERS TO THE EDITOR

MAGNETIC SUSCEPTIBILITY OF A ROOM TEMPERATURE LIQUID CRYSTAL (MBBA)

THIS paper reports the measurement of magnetic susceptibility of (*p*-methoxy benzalidene)-*p*-*n* butylaniline (abbreviated as MBBA) as it passes from liquid crystalline phase to isotropic liquid phase. The volume susceptibility was measured by Gouy's balance method¹. It is converted into mass susceptibility by dividing it by density of MBBA at required temperatures². Both H and H₀ were kept sufficiently large so that the nematic swarms may remain aligned completely in the direction of the field.

The variation of susceptibility with temperature is given in Fig. 1. MBBA is found to be a diamagnetic substance. The susceptibility drops suddenly at a temperature ~ 38°C. After 45°C the rate of variation of susceptibility is very slow.

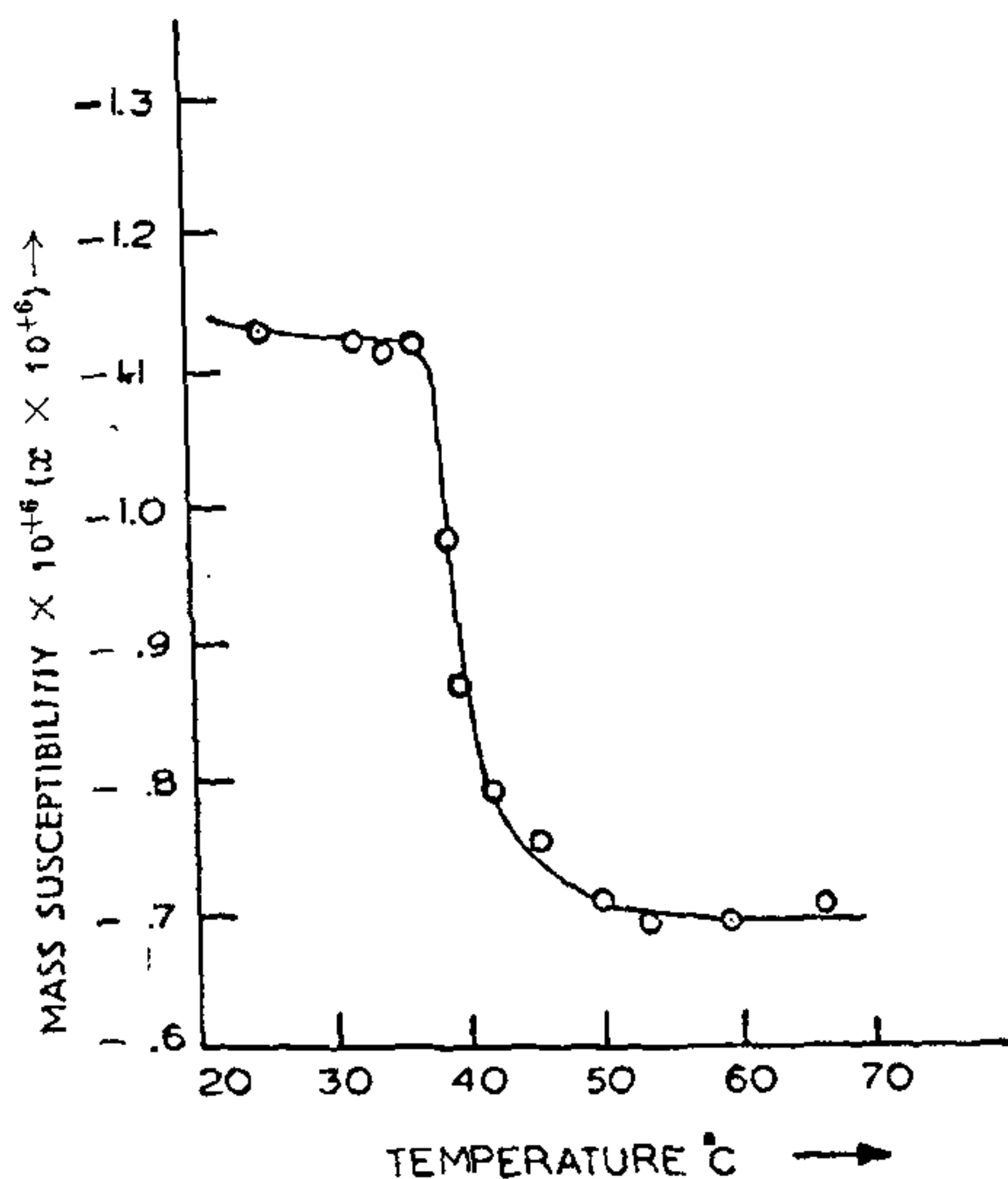


FIG. 1. Variation of mass susceptibility $\times 10^{+6}$ ($\chi \times 10^{+6}$) of MBBA vs temperature in °C.

Our optical measurements similar to Gray's³ measurements reveal that MBBA is a liquid crystal characterised by the following transition temperatures.

Solid 21°C Nematic Liquid Crystal 43°C Isotropic Liquid.

We would normally expect that in temperature range 21°–43°C the susceptibility variation would be slow because the material remains in the same phase. It is so upto a temperature ~ 38°C but then drops down suddenly, as such it appears that there is a pretransition disruption of liquid crystalline order. We conclude from our observation that nematic → isotropic transition temperature is the temperature at which maximum disruption of liquid crystalline order occurs and after which the disruption is very low. This may be explained on swarm hypothesis³, according to which nematic → isotropic transition temperature is the temperature at which big and ordered swarms are converted into very small cybotatic groups having much lesser degree of order of molecules. Our present measurements on MBBA show that there is a bigger change in susceptibility at transition temperature for MBBA as compared to *p*-azoxyanisole (PAA⁴) which means that field alignment in case of MBBA is easier.

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VIBRATIONAL SPECTRA OF N-METHYLTHIOPROPIONAMIDE AND N-DEUTERATED N-METHYLTHIOPROPIONAMIDE

THE Raman and infrared spectra of N-methylthioformamide and N-methylthioacetamide have been recorded by earlier workers and these molecules have been subjected to normal co-ordinate treatment^{1,2} in recent times in order to compare these

results with those of the corresponding ordinary secondary amides^{3,4}.

We now report the infrared and Raman frequencies of N-methylthiopropionamide and N-deuterated N-methylthiopropionamide. The infrared spectra of N-methylthiopropionamide and N-deuterated N-methylthiopropionamide and their solutions in chloroform were recorded using Perkin Elmer Model 337 Spectrophotometer. The Raman spectrum of N-methylthiopropionamide was

recorded with Coderg Raman spectrometer with a He-Ne laser source operating at 50 mw. The laser Raman spectrum thus recorded revealed a number of bands. These spectra are given in Figs. 1, 2 and 3. The infrared and Raman frequencies and of those of the functional groups of the thioamide and its deuterated species are given in Tables I and II. The frequencies of the functional groups of N-methylpropionamide and N-deuterated N-methylpropionamide are given in Table III for comparison.

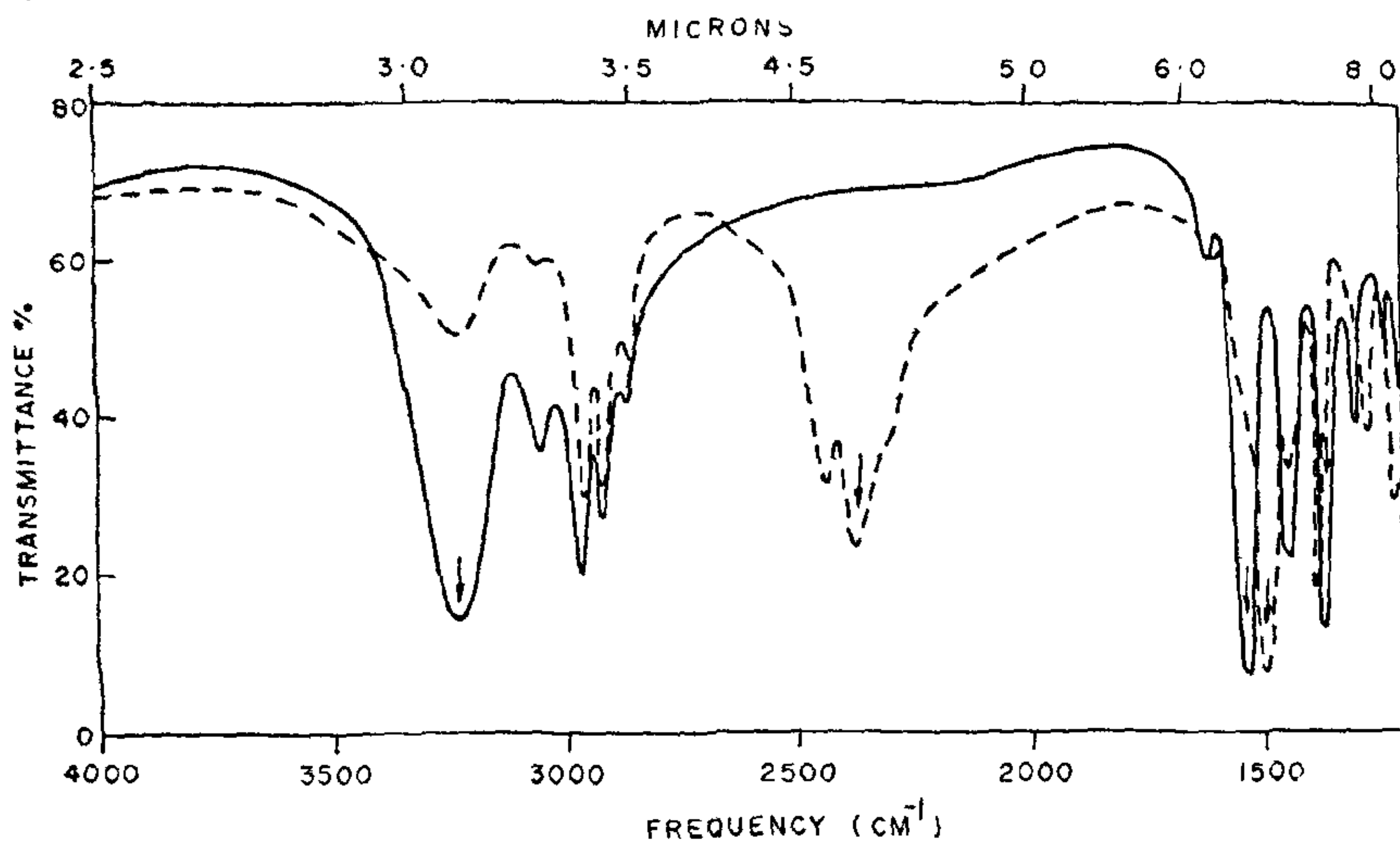


FIG. 1

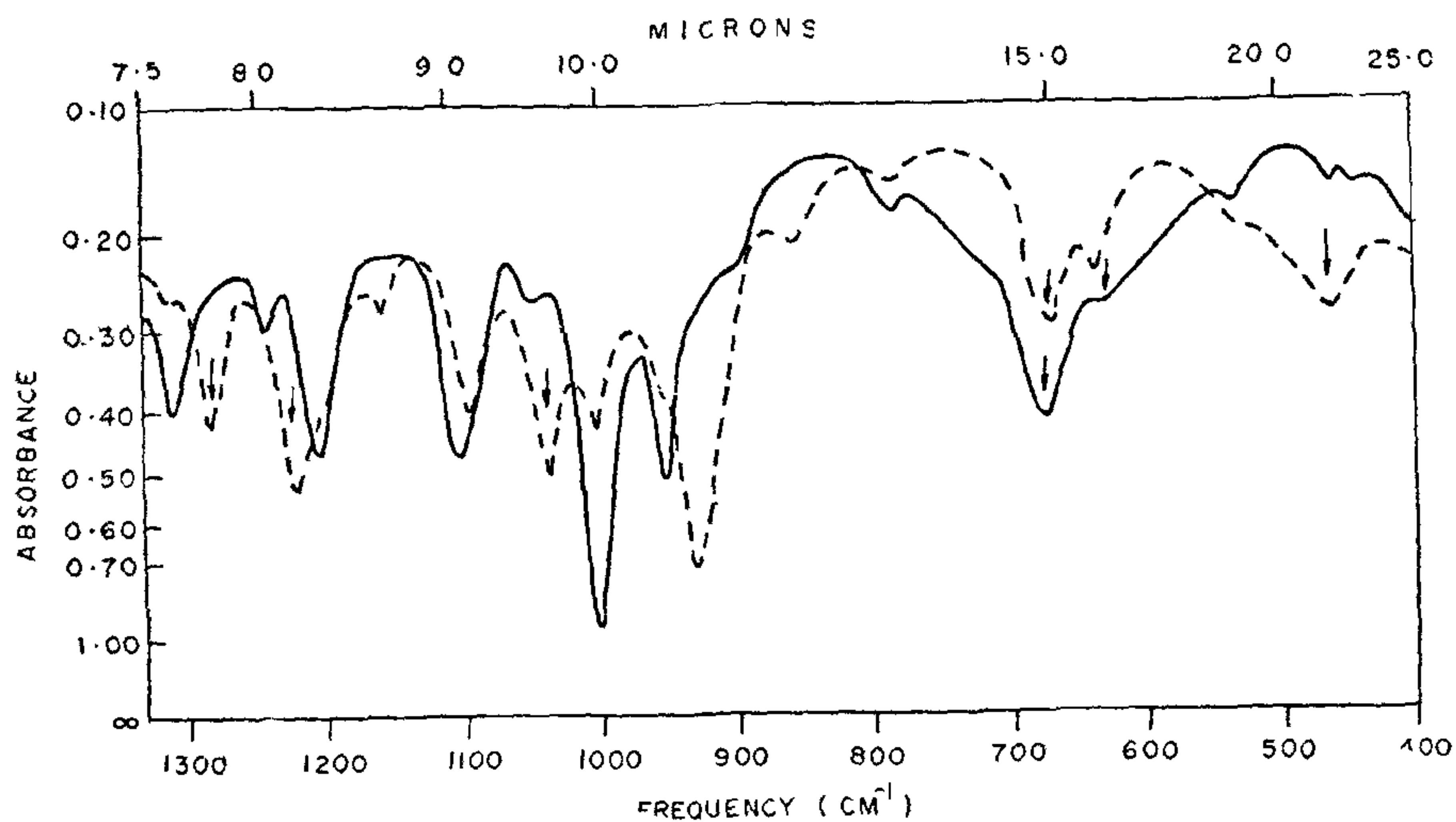


FIG. 2

FIGS. 1-2. Infrared spectra of N-methylthiopropionamide (Liquid film of unknown thickness)—Solid line and of N-deuterated N-methylthiopropionamide—Broken line.

Replacement of the hydrogen atom of the NH group by the deuterium was accomplished by adding

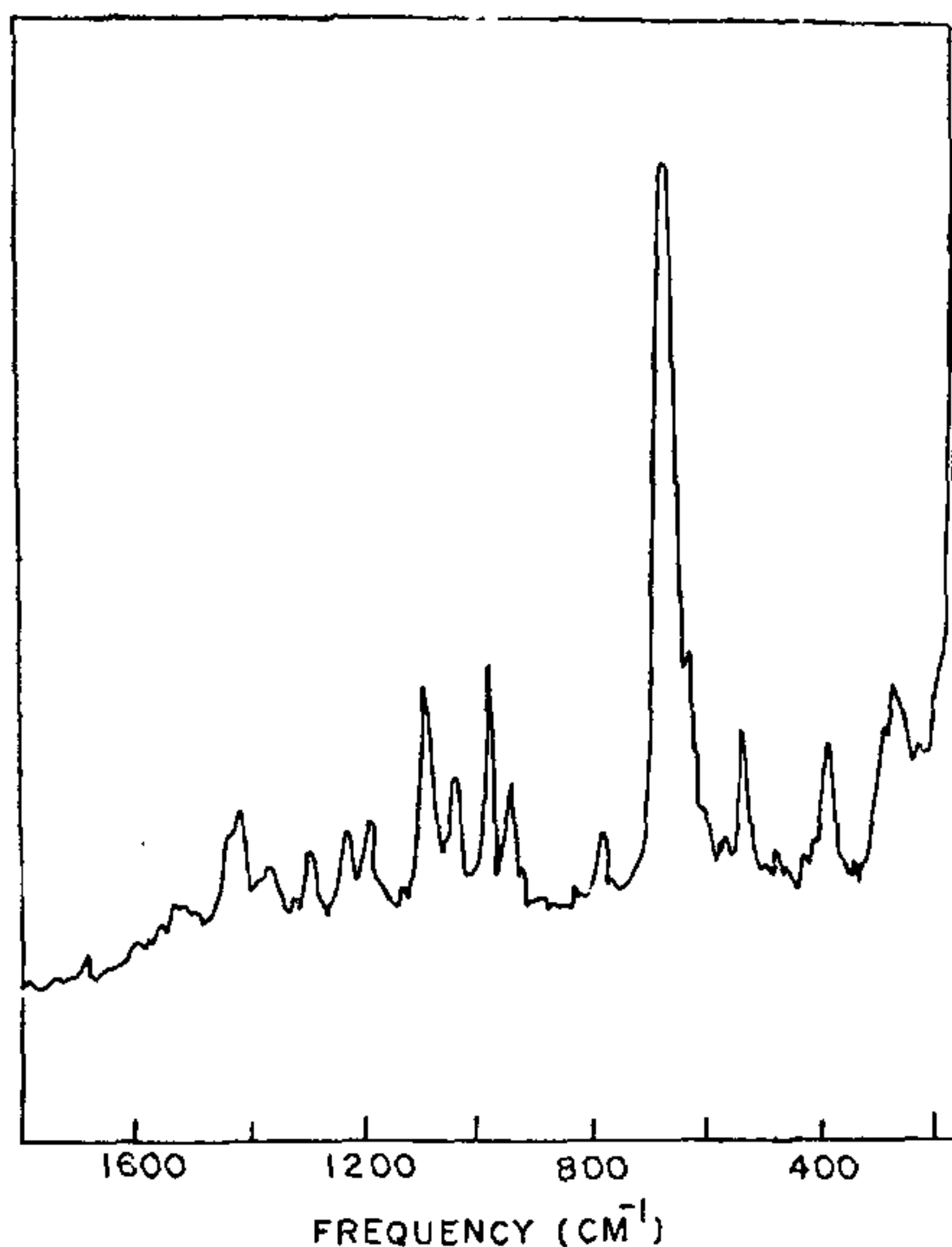


FIG. 3. Laser Raman spectrum of N-methylthiopropionamide.

TABLE I
Raman and infrared frequencies of N-methylthiopropionamide (frequencies in cm^{-1})

Raman	Infrared		Assignment
	Pure amide	In solution of $CHCl_3$	
..	..	3395 (VS)	ν (N—H) free
..	3225 (S, br)	..	ν (N—H) bonded
..	3060 (m)
..	2970 (ms)	2960 (ms)	ν_{as} (CH ₃) N
..	2925 (ms)	2925 (sh)	ν_{as} (CH ₃) C
..	2870 (w)	2850 (sh)	ν_s (CH ₃) N, C
1545 (w)	1540 (VS)	1515 (VS)	Amide II
1410 (m)	1438 (s)	1432 (ms)	δ_{as} (CH ₃) N, C
1375 (w)	1365 (s)	1362 (s)	Amide III
1290 (w)	1300 (ms)	1290 (w)	δ_s (CH ₃) N
1250 (m)	1235 (m)	..	δ_s (CH ₃) C
..	1204 (s)	1212 (ms)	..
1080 (m)	1100 (s)	1095 (m)	γ (CH ₃) N
..	1000 (VS)	1000 (VS)	γ (CH ₃) C
975 (m)	950 (m)	945 (m)	ν (C—CH ₃)
905 (w)	900 (w)	915 (w)	ν (N—CH ₃)
775 (w)	793 (w)	..	ν (C—CH ₂)
675 (vs)	688 (m)	670 (m)	ν (C=S)
..	630 (w)	630 (sh)	Amide IV
..	535 (VW)	555 (m)	δ (S=C—N)
480 (m)	455 (VW)	..	γ (C—CH ₃)
380 (m)	γ (C—CH ₂)
275 (m)	γ (N—CH ₃)

TABLE II

Infrared frequencies of the functional groups and of the amide III absorption band of N-methylthiopropionamide and N-deuterated N-methyl thiopropionamide (frequencies in cm^{-1})

N-Methylthiopropionamide			N-Deuterated N-Methylthiopropionamide		
Mode of vibration	Amide	In solution of $CHCl_3$	Mode of vibration	Amide	In solution of $CHCl_3$
ν (N—H) free	..	3395	ν (N—D)	..	2450
ν (N—H) bonded	3225	3225	ν (N—D)	2385	2395
ν (C=S)	688	670	ν (C=S)	670	670
Amide II	1540	1515	Amide II	1500	1490
.. III	1365	1360	.. III	1220	1220
.. IV	630 IV	465	..

TABLE III

Infrared frequencies of the functional groups and of the amide III absorption band of N-methylpropionamide and N-deuterated N-methylpropionamide (frequencies in cm^{-1})

N-Methylpropionamide				N-Deuterated N-Methylpropionamide		
Mode of vibration	Amide	In solution of CCl_4	Vapour	Mode of vibration	Amide	In solution of CCl_4
ν (N—H) free	..	3430	3430	ν (N—D)	..	2475
ν (N—D) bonded	..	3300	..	ν (N—D)	..	2417
Amide I	..	1650	1715	Amide I	..	1627
.. II	..	1545	1495	.. II	..	1475
.. III	..	1273	1258	.. III	..	1100
.. III	..	1238	1210	.. III	..	1100
.. IV	..	695	680	.. IV	..	500

three-fold excess of D_2O to the compound, pumping off the heavy water and repeating the process a number of times.

N-methylthiopropionamide molecule belongs to the point group C_s . The fundamental frequencies which are classified as eleven in-plane (A') and four out of plane (A'') vibrations are active both in the infrared and the Raman spectra. While the bands at 3395 cm^{-1} and 3225 cm^{-1} are assigned to the free and the bonded N-H stretching vibrations, the corresponding mode of vibration of the N-D linkage gives rise to absorptions at 2450 cm^{-1} and 2385 cm^{-1} . The amide II and the amide III absorption bands in N-methylthiopropionamide which are at 1540 cm^{-1} and 1365 cm^{-1} are due to the combined contribution of the δ (N-H) and ν (C-N) vibrations while the corresponding peaks in its deuterated species are at 1500 cm^{-1} and 1220 cm^{-1} respectively. A comparison of the observations in Tables II and III would indicate that the N-H and N-D stretching frequencies in N-methylthiopropionamide are lower and the frequency of the amide III band is higher than those of the corresponding absorptions in N-methylpropionamide. This pattern of variation is similar to the one observed in cases of N-methylthioacetamide^{1,2} and N-methylacetamide⁴. On the other hand, the frequency of the amide II band is almost the same in both N-methylthiopropionamide and N-methylpropionamide. The band at 675 cm^{-1} is assigned to the C=S stretching vibration and this is the strongest band in the laser Raman Spectrum. While the N-H stretch, the amide III and the amide IV absorption bands show considerable variation in their frequencies on deuteration, the change in the frequency of the amide II band is only about 40 cm^{-1} .

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INFRARED SPECTRUM OF 1-FLUORO-2 : 4-DINITROBENZENE

1-FLUORO-2 : 4-Dinitrobenzene is a trisubstituted benzene wherein three hydrogen atoms of benzene ring are replaced by a fluorine atom and two NO_2 groups. A study of the infrared spectrum of this molecule in liquid phase was undertaken to obtain

detailed information about the fundamental vibrations in the ground state.

The infrared spectrum of 1-Fluoro-2 : 4-Dinitrobenzene, contained in a cell, has been recorded in liquid phase in the region $4000\text{--}250\text{ cm}^{-1}$ on a Perkin Elmer double beam Infrared Spectrophotometer. The thickness of the liquid cell was 0.025 mm . The sample was obtained from B.D.H. Company, England, and was used without further purification. 67 bands have been observed and analysed in terms of various ground state vibrations.

1-Fluoro-2 : 4-dinitrobenzene molecule belongs to C_s point group having the plane of the molecule as the only element of symmetry. In this case there are two types of probable vibrations, namely, a' and a'' . a' vibrations are totally symmetric and give rise to polarised Raman lines whereas a'' vibrations are anti-symmetric and give rise to depolarised Raman lines. The analysis of the bands and the assignment of the fundamental frequencies have been done on the basis of comparison with those of similar molecules as neither the polarisation of Raman lines nor the shape of the infrared bands in vapour phase is known. The infrared trace of the molecule in the liquid phase is reproduced in Fig. 1 and the wavenumbers of the bands along with their probable assignments are given in Table I.

C-H stretching frequencies.—There are six C-H stretching frequencies in benzene with the following modes of vibrations :

$3062 (a_{1g})$, $3060 (b_{1u})$, $3047 (e_{2g})$ and $3080 (e_{1u})$.

The last two frequencies are doubly degenerate. In the case of trisubstituted benzenes only three C-H stretching frequencies are expected as the other three frequencies would depend upon the mass and nature of the substituents. Out of these three frequencies only two frequencies at 3095 and 3110 cm^{-1} have been observed with very strong intensities and have been assigned to C-H stretching mode of vibration.

C-H bending modes.—The C-H bending modes in substituted benzenes occur in two different frequency regions $1000\text{--}1300\text{ cm}^{-1}$ (in-plane bending) and $750\text{--}1000\text{ cm}^{-1}$ (out-of-plane bending modes). The six C-H in-plane bending modes are derived from a_{2g} (1340), b_{2u} (1152), e_{2g} (1178) and e_{1u} (1037) modes of benzene in which e_{2g} (1178) and e_{1u} (1037) are doubly degenerate. In the present case two frequencies at 1125 and 1148 cm^{-1} have been assigned to C-H in-plane bending mode of vibration. This interpretation finds support from the infrared spectrum of 2-chloro-4-nitroaniline in