

Vibrational spectra and normal coordinate analysis of N-methylthiopropionamide

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Abstract : The Raman spectrum of N-methylthiopropionamide was recorded in the region $100\text{--}4000\text{ cm}^{-1}$. The infrared spectra of N-methylthiopropionamide and N-deuterated N-methylthiopropionamide and their solutions in chloroform were also recorded in the range $4000\text{--}180\text{ cm}^{-1}$. Normal coordinate treatment of both N-methylthiopropionamide and N-deuterated N-methylthiopropionamide was carried out using general quadratic valence force field and the force constants were refined by the damped least squares method. The potential energy distributions in symmetry coordinates are discussed in relation to the mixing of skeletal frequencies for N-methylthiopropionamide and the nature of absorption band is investigated.

Vibrational spectroscopy has proved to be of much help in elucidating the structure of amides. Infrared and Raman spectra studies of dichroism, band contour studies and normal coordinate analysis of simple primary, secondary and tertiary amides and thioamides and of their deuterated species enabled various workers to assign the skeletal frequencies and to investigate the nature of amide I, amide II and the amide III absorption bands.

In this context, the vibrational spectra of N-methylthiopropionamide have been the object of much interest. IR and Raman spectra with tentative assignments were reported by Venkata Ramiah and Usha Bai [1]. However, the IR data was limited to 400 cm^{-1} , and Raman spectrum was limited between $200\text{--}1600\text{ cm}^{-1}$. The normal coordinate treatment of N-methylthiopropionamide was carried out by Raman Rao *et al* [2], but there is no report on the out-of-plane vibrations of both N-methylthiopropionamide and N-deuterated N-methylthiopropionamide.

Keywords : Vibrational spectra, N-methylthiopropionamide, N-deuterated thiopropionamide, vibrational assignment

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As there are several discrepancies in the assignments proposed in the above investigations [1,2], an attempt has been made to reinvestigate the Raman and infrared spectra by including both in-plane and out-of-plane vibrations. In the present work, we report a complete infrared and Raman data along with the results of normal coordinate analysis taking into account the internal modes of the CH_3 and CH_2 groups.

Table 1. Vibrational assignments of N-methylthiopropionamide and N-deuterated N-methylthiopropionamide.*

Species	Observed frequency		Vibrational assignments NMTP, deuterated NMTP	PED% NMTP, deuterated NMTP
	Infrared frequency and intensity NMTP cm ⁻¹	Infrared frequency for deuterated NMTP cm ⁻¹		
A'	3225 S	2380 MS	vN-H, vN-D	98S ₁ , 97S ₁
A'	2975 S	2970 MS	vasy(C ^{''} H ₃), vas(C ^{''} -H ₃)	99S ₂ , 99S ₂
A'	2925 MS	2930 MS	vasy(C ^{''} H ₃), vas(C'-H ₃)	97S ₃ , 93S ₃
A'	2873 VW	2865 VW	vsy(C ^{''} H ₃), vsy(C ^{''} -H ₃)	99S ₄ , 95S ₅
A'	2870 VW	2861 W	vsy(C ^{''} H ₃), vsy(C'-H ₃)	98S ₅ , 98S ₆
A'	2870 VW	2860 W	C ^{''} $\left\langle \begin{smallmatrix} H \\ H \end{smallmatrix} \right\rangle$ sym. stretch C ^{''} $\left\langle \begin{smallmatrix} H \\ H \end{smallmatrix} \right\rangle$ sym. str.	99S ₆ , 98S ₆
A'	1560 VS	1530 VS	C-N stretch, C-N stretch	44S ₇ , 18S ₃ , 20S ₁₁ , 16S ₂₃ , 68S ₇ , 21S ₁₁ , 18S ₂₃
A'	1435 MS	1435 W	C ^{''} H ₃ asym. deform, C ^{''} H ₃ asym. deform	72S ₈ , 10S ₁₀ , 81S ₈ , 12S ₁₀
A'	1430 VS	1427 VS	C ^{''} H ₃ asym. deform, C ^{''} H ₃ asym. deform	51S ₉ , 28S ₁₄ , 62S ₉ , 20S ₁₄
A'	1432 MS	1421 MS	C ^{''} $\left\langle \begin{smallmatrix} H \\ H \end{smallmatrix} \right\rangle$ bending, C ^{''} $\left\langle \begin{smallmatrix} H \\ H \end{smallmatrix} \right\rangle$ bending	21S ₁₁ , 15S ₈ , 40S ₁₀ , 31S ₁₁ , 14S ₈ , 52S ₁₀
A'	1365 W	1360 VW	C ^{''} H ₃ sym. deform, C ^{''} H ₃ sym. deform	68S ₁₁ , 15S ₁₀ , 65S ₁₁ , 21S ₁₀
A'	1359 MS	1370 MS	C ^{''} H ₃ sym. deform, C ^{''} H ₃ sym. deform	48S ₁₄ , 31S ₉ , 51S ₁₄ , 31S ₉
A'	1240 S	1230 MS	N-H deformation, N-D deformation	32S ₁₂ , 34S ₁₇ , 38S ₁₂ , 30S ₁₇
A'	1204 MS	1180 VW	C ^{''} H ₃ rocking, C ^{''} H ₃ rocking	68S ₁₅ , 21S ₂ , 61S ₁₅ , 20S ₂

Table 1. (Contd.)

Species	Observed frequency		Vibrational assignments NMTP, deuterated NMTP	PED% NMTP, deuterated NMTP	
	Infrared frequency and intensity NMTP cm ⁻¹	Infrared frequency for deuterated NMTP cm ⁻¹			
A'	1106 MS	1090 W	1080 M	C-H rocking, C-H ₃ rocking	40S ₁₃ , 20S ₁₇ , 38S ₁₃ , 22S ₁₇
A'	1003 VS	1000 W	-	$C'' \begin{pmatrix} H \\ H \end{pmatrix}$ wagging, $C'' \begin{pmatrix} H \\ H \end{pmatrix}$ wagging	42S ₁₆ , 21S ₁₉ , 42S ₁₆ , 28S ₁₉
A'	952 MS	928 VS	-	C-C'' stretch, C-C'' stretch	51S ₁₇ , 11S ₁₃ , 58S ₁₇ , 10S ₁₃ , 10S ₂₀
A'	-	860 VW	905 W	N-C'' stretch, C'''-N stretch	49S ₁₈ , 21S ₁₇ , 61S ₁₈ , 11S ₁₇
A'	790 VW	790 VW	775 W	C'-C'' stretch, C'-C'' stretch	58S ₁₉ , 20S ₁₇ , 56S ₁₉ , 21S ₁₇
A'	680 MS	671 VW	675 VS	C=S stretch, C=S stretch	38S ₂₀ , 11S ₂₄ , 45S ₂₀ , 15S ₂₇
A'	530 VW	529 VW	-	S=C-N deform, S=C-N deform	26S ₂₁ , 17S ₁₇ , 18S ₁₈ , 24S ₂₄ , 32S ₂₁ , 18S ₁₇ , 20S ₁₈ , 21S ₂₄
A'	480 VW	470 W	480 M	C'-C''-C deform, C'-C''-C deform	22S ₂₂ , 10S ₁₉ , 26S ₁₃ , 28S ₂₂ , 15S ₁₇ , 21S ₁₃
A'	380 VW	360 VW	380 M	C-C'' rock, C-C'' rock	32S ₂₃ , 15S ₁₉ , 38S ₂₃ , 21S ₁₉
A'	280 M	260 W	275 M	N-C'' rock, N-C'' rock	48S ₂₄ , 12S ₂₁ , 41S ₂₄ , 20S ₂₁
A''	2905 MS	2873 W	-	$\nu_{\text{asy}}(\text{CH}_3)_2$, $\nu_{\text{as}}(\text{CH}_3)_2$	97 $\nu_{\text{as}}(\text{CH}_3)_2$, 95 $\nu_{\text{as}}(\text{CH}_3)_2$
A''	2990 S	2867 W	-	$\nu_{\text{asy}}(\text{CH}_3)_2$, $\nu_{\text{as}}(\text{CH}_3)_2$	95 $\nu_{\text{asy}}(\text{CH}_3)_2$, 97 $\nu_{\text{as}}(\text{CH}_3)_2$
A''	-	2855 MS	2810 VS	$\nu_{\text{asy}}(\text{CH}_2)$, $\nu_{\text{as}}(\text{CH}_2)$	99 $\nu_{\text{asy}}(\text{CH}_2)$, 91 $\nu_{\text{as}}(\text{CH}_2)$
A''	1415 W	1390 W	1415 M	$\delta_{\text{asy}}(\text{CH}_3)_2$, $\delta_{\text{asy}}(\text{CH}_3)_2$	68 $\delta_{\text{asy}}(\text{CH}_3)_2 + 21\gamma(\text{CH}_3)_2$ 71 $\delta_{\text{asy}}(\text{CH}_3)_2 + 18\gamma(\text{CH}_3)_2$
A''	1413 W	1389 VW	-	$\delta_{\text{asy}}(\text{CH}_3)_2$, $\delta_{\text{asy}}(\text{CH}_3)_2$	64 $\delta_{\text{asy}}(\text{CH}_3)_2 + 17\gamma(\text{CH}_3)_2$ 67 $\delta_{\text{as}}(\text{CH}_3)_2 + 21\gamma(\text{CH}_3)_2$

Table 1. (Contd.)

Species	Observed frequency		Vibrational assignments NMTP, deuterated NMTP	PED% NMTP, deuterated NMTP
	Infrared frequency and intensity NMTP cm ⁻¹	Infrared frequency for deuterated NMTP cm ⁻¹		
A ^u	1410 W	1387 VW	$\delta_{asy}(\text{CH}_2)_2, \delta_{asy}(\text{CH}_2)$	$72 \delta_{asy}(\text{CH}_2)_2 + 15 \gamma(\text{CH}_2)$ $18 \gamma(\text{CH}_2) + 69 \delta_{as}(\text{CH}_2)$
A ^u	1165 W	1150 W	$\gamma(\text{CH}_3)_2, \gamma(\text{CH}_3)_2$	$54 \gamma(\text{CH}_3)_2 + 22 \delta_{asy}(\text{CH}_3)_2$ $69 \gamma(\text{CH}_3)_2 + 10 \delta_{as}(\text{CH}_2)$
A ^u	1150 W	1149 VW	$\gamma(\text{CH}_3)_2, \gamma(\text{CH}_3)_2$	$54 \gamma(\text{CH}_3)_2 + 22 \delta_{asy}(\text{CH}_3)_2$ $55 \gamma(\text{CH}_3)_2 + 25 \delta_{as}(\text{CH}_2)$
A ^u	1145 W	1119 W	$\gamma(\text{CH}_2), \gamma(\text{CH}_2)$	$71 \gamma(\text{CH}_2) + 26 \delta_{asy}(\text{CH}_2)$ $75 \gamma(\text{CH}_2) + 11 \delta_{as}(\text{CH}_3)_2$
A ^u	985 W	980 W	$\omega(\text{CH}_3)_2, \omega(\text{CH}_3)_2$	$59 \omega(\text{CH}_3)_2 + 10 \tau(\text{CH}_3)_2$ $60 \omega(\text{CH}_3)_2 + 12 \tau(\text{CH}_3)_2$
A ^u	-	979 VW	$\omega(\text{CH}_3)_2, \omega(\text{CH}_3)_2$	$51 \omega(\text{CH}_3)_2 + 15 \tau(\text{CH}_3)_2$ $51 \omega(\text{CH}_3)_2 + 18 \tau(\text{CH}_3)_2$
A ^u	970 M	970 W	$\omega(\text{CH}_2), \omega(\text{CH}_2)$	$49 \omega(\text{CH}_2) + 21 \tau(\text{CH}_2)$ $54 \omega(\text{CH}_2) + 15 \tau(\text{CH}_2)$
A ^u	223 M	-	$\tau(\text{CH}_3)_2, \tau(\text{CH}_3)_2$	$54 \tau(\text{CH}_3)_2 + 29 \omega(\text{CH}_3)_2$ $49 \tau(\text{CH}_3)_2 + 22 \omega(\text{CH}_3)_2$
A ^u	188 W	188 W	$\tau(\text{CH}_3)_2, \tau(\text{CH}_3)_2$	$48 \tau(\text{CH}_3)_2 + 19 \omega(\text{CH}_3)_2$ $41 \tau(\text{CH}_3)_2 + 18 \omega(\text{CH}_3)_2$
A ^u	-	180 W	$\tau(\text{CH}_2), \tau(\text{CH}_2)$	$42 \tau(\text{CH}_2) + 24 \omega(\text{CH}_2)$ $52 \tau(\text{CH}_2) + 26 \omega(\text{CH}_2)$

v - Stretch δ - deformation β - bending γ - rocking ω - wagging τ - torsion

* The symmetry coordinates (S) are available from the authors.

Pure chemicals of N-methylthiopropionamide (NMTP) obtained from Bharathidasan University was used as such without further purification, to record Raman and infrared spectra. The laser Raman spectrum of NMTP was recorded using 488 nm line of Ar⁺ for excitation in the region 100–4000 cm⁻¹ in Cary Model grating spectrophotometer with a 4 W Ar⁺ laser. The infrared spectrum of NMTP and N-deuterated NMTP and their solutions in chloroform were recorded using Perkin Elmer 983G double beam grating spectrophotometer. N-deuteration was achieved by repeated exchanges with D₂O. The removal of D₂O was carried out at room temperature in order to minimize a possible sample deterioration which was reported in literature [3]. Experiments carried out under the same conditions used for the deuterium exchange, but using normal water as solvent, did not reveal detectable sample changes.

In order to ascertain the amount of mixing among the normal modes and to obtain a more accurate description of the fundamental vibrations of NMTP and N-deuterated NMTP, a normal coordinate analysis was undertaken. The calculations were performed using Wilson's FG matrix method with the computer programs developed by Schachtschneider [4].

The molecular skeleton is planar to a good approximation and therefore a C_s symmetry can be assumed. This results in 39 fundamental vibrations which span the irreducible representations as 24A' (in-plane) and 15A'' (out-of-plane) vibrations. All the fundamental modes are active in both Raman and infrared spectra. The bond lengths used in the present investigation are C–N = 1.36 Å; C = S = 1.71 Å; N–C = 1.47 Å; C–C = 1.54 Å; C–H = 1.09 Å and N–H = 1.02 Å. These values are taken from similar related system in reference to the title molecule.

The observed and calculated frequencies, potential energy distributions (PED) in symmetry coordinates for NMTP and N-deuterated NMTP are shown in Table 1. PED in symmetry coordinates is obtained by using the formula $F_{ii}L_{ik}^2 / \lambda_k$. PED contributions below 10% are not shown in the table.

References

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