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Vibrational Spectra and Normal Coordinate Analysis of *N*-Methyl Thiourea

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The infrared spectra of *N*-methylthiourea (NMTU) and its *N*-deuterated and *S*-methylated species were measured. Assignment of the infrared and Raman spectra of NMTU has been accomplished by correlation with thiourea and by use of infrared band shifts on *N*-deuteration as well as *S*-methylation. Normal coordinate analysis was performed for all the fundamentals of NMTU and NMTU-d_3, the assignments obtained from the force field calculations being discussed in relation to those in other related thioureas and thioamides. The potential barriers to the internal rotations for the $-NH_2$, $-CH_3$, and $-CN$ groups were estimated from the force constants.

There is continued interest in the study of thiourea derivatives and their metal complexes in recent years. This may be due to some unusual spectroscopic, magnetic and structural properties shown by the metal complexes of thiourea derivatives as well as to the potential ability of thioureas for ambidentate coordination.[1–4)]

N-Methylthiourea (NMTU) is the simplest alkyl-substituted thiourea. An analysis of its vibrational spectrum is necessary for the investigation of the characteristic frequencies and the force field of thiourea derivatives. Lane *et al.*[4)] tentatively assigned the infrared spectra of NMTU in the region 4000—700 cm^{-1}. Of particular interest is their assignment of the C=S stretching frequency at 780 cm^{-1}. Jensen and Nielsen,[5)] however, attributed a band near 635 cm^{-1} to a coupled C=S stretching mode. There are differences in the assignments also of other bands for NMTU. No complete assignment of the infrared spectra of *N*-methyl thiourea is available although quantitative vibrational assignments of thiourea,[6–8)] *N,N'*-dimethyl-,[9,10)] and tetramethylthioureas[10,11)] have been accomplished by normal coordinate treatments. Recently, detailed vibrational assignments for thiosemicarbazide[12,13)] ($H_2HNH-C(=S)-NH_2$) and *N*-methylurea[14)] (NMU), closely related to NMTU, have been published.

An appropriate description of the fundamental vibrations of NMTU arrived at with the aid of normal coordinate analysis of NMTU and NMTU-d_3 and the infrared spectrum of the *S*-methylated NMTU is discussed herewith. The potential barriers to the internal rotation about C–N and C–C bonds are estimated from the force constants.

Experimental

NMTU was prepared by the method of Moore and Crossley[15)] and purified by recrystallization from absolute ethanol. NMTU-d_3 was obtained by dissolving NMTU in D_2O and evaporating the excess D_2O in vacuo. The process was repeated several times till the infrared spectrum showed no bands due to NH vibrations. The *S*-methyl derivative of NMTU was prepared by the procedure of Brand and Brand.[16)]

Spectra: Infrared spectra were measured on a Carl Zeiss UR 10 spectrophotometer between 4000 and 400 cm^{-1} in Nujol mull and KBr pellet. Far infrared spectra from 400 to 30 cm^{-1} were recorded on a Polytec FIR 30 spectrometer as polyethylene pellet. The Raman frequencies of NMTU are quoted from recent data.[17)]

Normal Coordinate Treatment. The GF matrix method of Wilson[18)] was employed. A trans-planar –CSNH– conformation supported by nuclear magnetic resonance studies[19)] with a molecular symmetry C_s was adopted. The 27 vibrations of NMTU then divide themselves into 18 a′ (in-plane) and 9 a″ (out-of-plane) modes, all being infrared and Raman active. The following molecular parameters transferred from those of NMU[14)] and Pt(II) *N*-ethyl thiourea complex[1)] were used: bond distances N–H 1.00; C–H 1.08; C′–N 1.465; C–N 1.351; C–S 1.73 Å. The angles around the methyl carbon atom were taken to be tetrahedral (109.47°) and those around the nitrogen of the NH_2 group 120°. The other angles were -NCN 117°; NCS and N′CS 121.5°; C′NH and CN′H 120°. The molecular structure and the internal coordinates are shown in Fig. 1. The symmetry coordinates were the same as those employed for NMU.[14,20)]

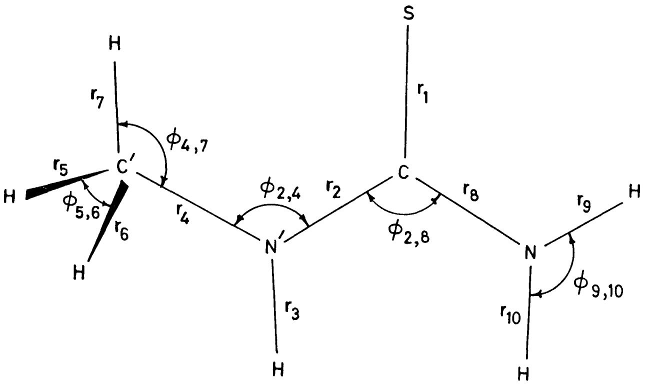

Fig. 1. Structure and internal coordinates of *N*-methyl thiourea.

The Urey-Bradley force field which gives satisfactory explanation of the spectra of thioamides[21–23)] and thioureas[6,8,10)] was employed. To begin with, zeroth order calculations were performed for the planar vibrations using the force constants transferred from (a) thioacetamide[21)] (TAM), and (b) thiourea[6)] (TU) and thioacetamide.[21)] The zeroth order frequencies were similar in both cases and were reasonably close to the observed frequencies, the potential energy distributions (PED) being also comparable. For out of plane vibrations, the methyl group was treated by the Urey-Bradley force function, the valence force constants being employed for the planar molecular skeleton. The initial values of the valence force constants were taken from NMU.[14)]

The force constants of set (a) were refined in order to get a good agreement between the calculated and observed frequencies for both NMTU and NMTU-d_3. The final force constants given in Table 1 are comparable with those of the initial ones, requiring only minor modifications.

Table 1. Force constants[a)] for *N*-methylthiourea

Stretching		Bending		Repulsive	
K	NMTU	H	NMTU	F	NMTU
CS	4.10	HNH	0.41	HNH	0.0
CN	5.30	HNC	0.30	HNC	0.55
CN′	5.10	NCS	0.36	NCS	1.05
NH	5.60	NCN	0.74	NCN	0.65
N′H	5.10	N′CS	0.45	N′CS	1.10
C′N	2.65	CN′H	0.12	CN′H	0.50
CH	4.45	CNC	1.20	CNC	0.30
		HNC′	0.07	HNC′	0.95
		NC′H	0.27	NC′H	0.50
		HCH	0.43	HCH	0.04

Valence constants[b)]

$f(\mathrm{wNH_2})$	0.056	$f(\pi\mathrm{NH})$	0.060	$f(\mathrm{wNH_2}, \pi\mathrm{NH})$	−0.008
$f(\tau\mathrm{NH_2})$	0.110	$f(\tau\mathrm{CN})$	0.095	$f(\tau\mathrm{CN}, \pi\mathrm{NH})$	−0.022
$f(\pi\mathrm{CS})$	0.090	$f(\tau\mathrm{CH_3})$	0.006		

a) K, H, and F are in mdyn/Å and the valence constants (f) in mdyn Å. Intramolecular tension $k(\mathrm{CH_3})$ −0.05 mdyn Å and interaction constant $P(\mathrm{NH, NH})$ −0.12 mdyn/Å. b) w, τ, and π: As in Table 2.

The computations were carried out on an IBM 360/44 computer using programs similar to those of Schachtschneider.[24)]

Results and Discussion

Agreement between the observed and calculated frequencies for NMTU-d_0 and -d_3 is satisfactory. The somewhat larger deviations for the deuterated compound can be attributed to the higher anharmonicity associated with the hydrogen-involving vibrations. As usual,[25)] an interaction constant, P(NH,NH), was employed to get a better fit for the $\mathrm{NH_2}$ stretching frequencies.

Band Assignments. The observed and calculated frequencies and an approximate description of the vibrations derived from the potential energy distributions amongst the symmetry coordinates are given for NMTU and NMTU-d_3 in Tables 2 and 3, respectively.

Alternate assignments for the frequencies below 700 cm^{-1} were considered by means of force field calculations. Final selection consistent with a satisfactory interpretation of all the bands was made by referring to the deuterium frequency shifts and the characteristic group frequencies in structurally related molecules.

In-plane Vibrations. *Thioureide Group Vibrations. NH, NH_2 Stretching*: The infrared spectrum of NMTU shows three bands in the region above 3000 cm^{-1} assignable to $\mathrm{NH_2}$ and NH stretching vibrations. The bands at 3350 and 3189 cm^{-1} are easily assigned to asymmetric and symmetric $\mathrm{NH_2}$ vibrations,respectively, and the band at 3280 cm^{-1} to NH stretching. On deuteration these bands are replaced by new ones at 2520, 2350, and 2415 cm^{-1}, respectively.

CN Stretching: According to the normal coordinate analysis, the band at 1567 cm^{-1} (near 1555 cm^{-1} in Raman) assigned by Lane *et al.*[4)] to the thioamide II band of the –CSNH– group is due to a highly coupled vibration comprising of CN and CS stretching and NCN and CNC bending modes. The band as expected shifts to a higher frequency on *S*-methylation, being observed at 1590 cm^{-1} in the spectrum of *N*,*S*-dimethyl thiourea hydroiodide.

Table 2. Observed and calculated fundamentals and assignments for *N*-methylthiourea

Frequency, cm^{-1}			D[c)]	Assignment[a)] (Potential energy distributions,[b)] %)
Obsd		Calcd		
Raman	IR			
a′ species				
3325	3350	3357	0.2	$\nu_a\mathrm{NH_2}$ (100)
3293	3230	3274	0.2	νNH (99)
3166	3139	3193	0.1	$\nu_s\mathrm{NH_2}$ (99)
2925	2970	2972	0.1	$\nu_a\mathrm{CH_3}$ (99)
2873	2880	2888	0.3	$\nu_s\mathrm{CH_3}$ (99)
1628	1642	1639	0.2	$\delta\mathrm{NH_2}$ (82)
1554	1567	1573	0.4	ν_sCN (23), δNCN (22), νCS (19)
1488	1500	1503	0.2	ν_aCN (60)
1428	1462	1456	0.4	$\delta_a\mathrm{CH_3}$ (75)
1406	1408	1394	1.0	$\delta_s\mathrm{CH_3}$ (79)
1296	1302	1301	0.1	δNH (65)
1145	1154	1139	1.3	$\mathrm{rNH_2}$ (53)
1126	1125	1122	0.3	νC′N (53), ν_sCN (25)
973	980	1000	2.0	$\mathrm{rCH_3}$ (46), $\mathrm{rNH_2}$ (18)
767	778	768	1.3	νCS (64)
	635	657	3.5	δSCN (27), δCNC (23), νC′N (23)
487	496	494	0.4	δNCN (52), δSCN (20)
280	300	294	2.0	δCNC (39), δSCN (38)
a″ species				
3003	2970	2969	0.0	$\nu\mathrm{CH_3}$ (100)
	1460	1461	0.1	$\delta\mathrm{CH_3}$ (85)
		1043		$\mathrm{rCH_3}$ (82)
700	725	712	1.8	$\tau\mathrm{NH_2}$ (99)
594	600	587	2.2	$\mathrm{wNH_2}$ (91)
574	557	547	1.8	τCN (48), πNH (42)
406	400	403	0.8	πCS (75)
194	185	187	1.1	πNH (57), τCN (27)
	135	135	0.0	$\tau\mathrm{CH_3}$ (87)

a) ν, stretching; a, asymmetric; s, symmetric; δ, bending; r, rocking; w, wagging; τ, torsion and π, out-of-plane bending. b) $100L_{ik}^2F_{ii}/\lambda_k$; those less than 20% are omitted when the individual or sum of the PED is higher than 50%. c) D is the deviation of ν as a percentage:

$$D = (|\nu_{\mathrm{obsd}} - \nu_{\mathrm{calcd}}|) \times 100/\nu_{\mathrm{obsd}}.$$

The 1500 cm^{-1} band (at 1488 cm^{-1}, Raman spectrum) may be chiefly associated with C–N asymmetric stretching, which is higher than that in thiourea[6)] assigned to 1472 cm^{-1}. The 1500 cm^{-1} band of NMTU is unaffected in the *S*-methyl derivative except for an increase in intensity.

NH, NH_2 Bending: Thereis a doublet in the infrared spectrum of NMTU in the 1250—1300 cm^{-1} region; the band at 1302 cm^{-1} is strong and that at 1262 cm^{-1} is medium in intensity. In the Raman spectrum also a strong band at 1296 cm^{-1} and a medium shoulder band at 1260 cm^{-1} are observed. The strong band at 1302 cm^{-1} is taken as the fundamental and the one at 1262 cm^{-1} may be due to an overtone, enhanced in intensity possibly due to Fermi resonance with the fundamental at 1302 cm^{-1}.

TABLE 3. OBSERVED AND CALCULATED FUNDAMENTALS AND ASSIGNMENTS FOR *N*-METHYLTHIOUREA-d_3

Frequency, cm^{-1} Obsd	Frequency, cm^{-1} Calcd	D	Assignment (Potential energy distributions, %)
a′ species			
2970	2972	0.1	$\nu_a CH_3$ (99)
2880	2889	0.3	$\nu_s CH_3$ (99)
2520	2489	1.2	$\nu_a ND_2$ (98)
2415	2393	0.9	νND (97)
2350	2305	1.9	$\nu_s ND_2$ (97)
1545	1518	1.7	$\nu_s CN$ (25), δNCN (19), νCS (18)
1512	1493	1.3	$\nu_a CN$ (52)
1460	1452	0.5	$\delta_a CH_3$ (67)
1395	1381	1.0	$\delta_s CH_3$ (91)
1195	1223	2.3	δND_2 (68)
1130	1130	0.0	rCH_3 (43)
1080	1079	0.1	$\nu C'N$ (51)
954	919	3.7	δND (55), rCH_2 (29)
870	860	1.1	rND_2 (62)
708	731	3.2	νCS (68)
630	630	0.0	$\nu C'N$ (23), δCNC (22), $\nu_s CN$ (21), δSCN (21)
451	444	1.6	δNCN (47), δSCN (24)
292	292	0.0	δSCN (37), δCNC (39)
a″ species			
2970	2969	0.0	νCH_3 (100)
1460	1461	0.0	δCH_3 (85)
1075	1043	3.0	rCH_3 (82)
510	517	1.3	τND_2 (77)
475	495	4.2	wND_2 (50), πCS (31)
420	416	1.0	πND (41), τCN (22), wND_2 (20)
360	352	2.2	τCN (43), τCS (30)
184	178	3.2	πND (51), τCN (27)
130	135	3.8	τCH_3 (86)

The present assignment of the 1302 cm^{-1} band to thioamide II band of the –CSNH– group agrees qualitatively with that of Lane *et al.*[4] According to the potential energy distribution, the 1302 cm^{-1} band arises mainly from N–H bending (65%). This band (as also does the 1262 cm^{-1} band) disappears on N-deuteration, a new band at 954 cm^{-1} due to ND bending being found in the spectrum of NMTU-d_3. The NH bending frequency of NMTU is lower than the one at 1354 cm^{-1} in NMU.[14]

The thioamide II band of the –CSNH$_2$ group due to NH$_2$ bending is observed at 1642 cm^{-1}.

NH$_2$ Rocking: The band at 1154 cm^{-1} may be assigned to a coupled NH$_2$ rocking. It is compatible with the 1160 cm^{-1} band of NMU. That the 1154 cm^{-1} band of NMTU undoubtedly has its origin in the NH$_2$ group is confirmed by deuteration studies. It shifts to 870 cm^{-1} in the infrared spectrum of NMTU-d_3. The normal coordinate analysis shows the 1125 cm^{-1} band as due to a mixed mode mainly of H$_3$C–N and symmetric C–N stretching vibrations.

CS Stretching: There are two bands in the infrared spectrum of NMTU, a strong sharp band at 778 cm^{-1} and a strong somewhat broad band at 725 cm^{-1}. In the present investigation, the 778 cm^{-1} band is assigned to the C=S stretching in line with that of Lane *et al.*[4] and the 725 cm^{-1} band to an out-of-plane NH$_2$ bending. According to the potential energy distribution, the C=S stretching contributes nearly 65% to the 778 cm^{-1} band. A very intense Raman band at 767 cm^{-1} is observed in support of this assignment. Further, if the 778 cm^{-1} band is assigned to the NH$_2$ out-of-plane bending, the calculated frequency for the corresponding ND$_2$ mode is at 570 cm^{-1}, whereas a new strong band observed on N-deuteration is at 510 cm^{-1}.

The assignment of C=S stretching (Thioamide I band) of NMTU at 778 cm^{-1} is comparable with the C=S stretching frequency in the isoelectronic thiosemicarbazide[10,11] assigned to 800 cm^{-1}. Similarly, *N*-ethylthiourea also exhibits a strong Raman band[17] in this region at 806 cm^{-1}, which may be assigned to the C=S stretching mode. Thus the C=S stretching frequency of NMTU is higher than that in thiourea[6] and *sym-N,N′*-dimethylthiourea[9,10] assigned near 730 cm^{-1}. As in NMTU, strong Raman bands are also observed near 730 cm^{-1} in these compounds. The 778 cm^{-1} band is nearly unaffected on *S*-methylation, the behavior being similar to the *S*-methylation of thiourea. The 727 cm^{-1} band of thiourea predominantly due to C=S stretching is unaffected in the spectrum of the *S*-methyl derivative.[5]

The C=S stretching vibration has been empirically assigned to 635 cm^{-1} by Jensen and Nielsen[5] from a comparison of the spectrum of NMTU with that of it seleno analogue. This is not supported by normal coordinate analysis. However, the 635 cm^{-1} band has contribution from NCS bending and therefore shifts to a lower frequency on selenation which explains their observation.

Skeletal Bending: The band at 496 cm^{-1} is due to NCN bending, a band assigned similarly being found at 487 cm^{-1} in thiourea.[6] The NCS bending occurs as a coupled mode, contributing to the bands at 635, 496 and 300 cm^{-1}. In contrast, TAM exhibits a nearly pure NCS bending vibration[21] near 470 cm^{-1}. The zeroth order calculations clearly showed the 635 cm^{-1} band to be a coupled vibration of NCS and CNC bending modes. The lowest in-plane fundamental at 300 cm^{-1} can be assigned to CNC bending as in NMU.[14]

Methyl Group Vibrations. The band at 980 cm^{-1} can be assigned to CH$_3$ rocking which is coupled with NH$_2$ rocking as in TAM.[21] The assignment differs from that of Lane *et al.*[4] who have attributed CH$_3$ rocking to 1154 and 1125 cm^{-1} bands (considered as a doublet). As expected, the 980 cm^{-1} band is absent in thiourea.[6] The other CH$_3$ group vibrations are easily assigned as shown in Tables 2 and 3.

Out-of-plane Vibrations. There are five a″ modes for the planar skeleton. The NH$_2$ torsional mode of NMTU assigned to 725 cm^{-1}, which on deuteration shifts to 510 cm^{-1}, is compatible with that of NMU[14] and TAM[21,22] where it has been assigned near 710 cm^{-1}. The 600 cm^{-1} band of NMTU arises from NH$_2$ wagging. This is lower than the NH$_2$ wagging in TAM[19,20] at 709 cm^{-1} but higher than that in NMU[14] at 531 cm^{-1} and in urea[26] at 555 cm^{-1}.

The potential energy distributions show the NH bending (thioamide V band) to be highly mixed with

CN torsion, contributing to the bands at 557 and 185 cm^{-1}. A similar coupling of NH bending with CN torsion has been noted for diacetamide.[27] The band at 400 cm^{-1} of NMTU is attributed to the C=S out of plane bending (thioamide VI band). The CH_3 torsion is associated with a band at 135 cm^{-1} which is lower than that in NMU[14] at 166 cm^{-1}.

Internal Rotation. The potential barriers for the internal rotation about the C–N bonds, V_{NH_2} and V_{CH_3}, of the $-CSNH_2$ and the $-NHCH_3$ groups, respectively, can be approximated from the values of the respective torsional force constants. Using the treatment employed for NMU[14] and acetamide,[25] the barrier heights can be calculated from the relation

$$V_{NH_2} = 2f(\tau NH_2) = 30.7\ \text{kcal mol}^{-1}$$

and

$$V_{CH_3} = 3/4f(\tau CH_3) = 0.6\ \text{kcal mol}^{-1}.$$

The values of V_{NH_2} and V_{CH_3} are comparable with those of NMU[14] (31.3 and 1.7 kcal mol^{-1}, respectively). Similarly the barrier to the internal rotation about the CN bond of the –CSNH– group is given by

$$V_{CN} = 2f(\tau CN) - \Delta V/4 = 26.0\ \text{kcal mol}^{-1},$$

where ΔV is the energy difference between the *cis*- and *trans*-isomers of NMTU estimated to be 9.0 to 12.0 kcal mol^{-1} by the NMR method.[19] By taking ΔV as 9.0 kcal mol^{-1}, the value obtained for V_{CN} of NMTU is comparable with that of NMU[12] and *N*-methylformamide[28] (25.6 and 28.0 kcal mol^{-1}, respectively).

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