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Assignment of Fundamental Vibrations of *N,N'*-Dimethylthiourea

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The infrared spectra of symmetric *N,N'*-dimethylthiourea (s-DMTU) and its *N*-deuterated (s-DMTU-d_2) species have been measured. The fundamental frequencies have been assigned by comparison with the assignments in structurally related molecules and the infrared band shifts on *N*-deuteration, *S*-methylation, available Raman data and with the aid of theoretical band assignments from normal coordinate treatments for s-DMTU-d_0 and -d_2. A force field is derived for s-DMTU by transferring the force constants chiefly from *N*-methylthiourea and the subsequent refinement of the force constants by a least squares procedure.

There is continued interest in the vibrational spectra of thiourea derivatives. The infrared and Raman spectra and normal coordinates of thiourea (TU)[1-3] and its *N*-methyl compounds namely, *N*-methylthiourea (NMTU),[4] unsymmetric *N,N*-dimethylthiourea (u-DMTU),[5] and *N,N,N',N'*-tetramethylthiourea (TMTU)[6,7] have been published. In this context, it was felt desirable to obtain a more complete assignment for symmetric *N,N'*-dimethylthiourea (s-DMTU), and compare the results with its oxygen analogue, symmetric *N,N'*-dimethylurea (DMU),[8] and with thiocarbohydrazide (TCH, $H_2NNHCSNHNH_2$),[9] with which it is isoelectronic.

The infrared spectrum of s-DMTU was previously reported by Rao *et al.*[7] These authors have also carried out a normal coordinate treatment for only the in-plane vibrations employing a point mass approximation for the methyl group on a molecular model with a point group symmetry C_{2v}. Afterwards, Ritchie *et al.*[10] reinvestigated the vibrational spectra of s-DMTU-d_0 and -d_2 and performed a vibrational analysis for mainly the in-plane vibrations also assuming a molecular symmetry C_{2v}. However, they point out that the available Raman depolarization data suggests that the molecule is likely to have a lower molecular symmetry (C_s). There are some significant differences between the assignments of Rao *et al.* and Ritchie *et al.* And further, a complete interpretation of the vibrational spectra of this interesting molecule is lacking.

The results of the force field calculations for all the fundamentals of s-DMTU-d_0 and -d_2 are presented for the more stable *cis-trans* conformation in this paper. The present assignments for s-DMTU are compared with the earlier ones and are discussed in relation to the assignments available for other thioureas and related compounds. In order to obtain some support for the C=S and C–N stretching bands from the band shifts, the infrared spectrum of the *S*-methyl derivative of s-DMTU is also studied.

Experimental

s-DMTU was synthesized starting from methyl isothiocyanate and methylamine.[11] It was recrystallized from dry ethanol mp 62°.

s-DMTU was *N*-deuterated by dissolving it in D_2O and evaporating the solution *in vacuo*. The process was repeated several times till the infrared spectrum showed practically no bands due to NH vibrations. The *S*-methyl derivative of s-DMTU was prepared according to the method of Brand and Brand.[12] It was dried under vacuo over phosphorus pentaoxide.

Spectra: The infrared spectra were measured on a Carl-Zeiss UR 10 spectrophotometer in the range 4000 to 400 cm^{-1} by Nujol mull and KBr pellet techniques. The bands in the far infrared region and also the Raman frequencies were taken from the recently published spectra.[13] The solution infrared spectra in $CHCl_3$ were recorded for different concentrations between 4000—500 cm^{-1} using NaCl windows of path length 0.4 mm.

Normal Coordinate Analysis

Wilson's GF matrix method was employed.[14] A stable *cis-trans* conformation may be expected for s-DMTU.[10,15-19] The molecular geometry for s-DMTU was constructed on the basis of the results of the X-ray diffraction structural information on the metal complexes[18,19] of s-DMTU and free TMTU.[20] The molcular parameters employed are, C=S 0.171, C–N 0.133, N–CH_3 0.147, C–H 0.109, N–H 0.101 nm, HCH, HCN 109°28′, and all interbond angles of 120° for the planar skeleton.

The 36 normal modes of s-DMTU are classified in the point group C_s into 23 of species a′ (in-plane) and 13 of species a″ (out-of-plane) vibrations. All the normal modes are infrared and Raman allowed. The internal displacement coordinates are shown in Fig. 1, and the symmetry coordinates employed are not listed here for the sake of brevity. A simple Urey-Bradley force field (UBFF) was employed. For the out of plane vibrations of the planar skeleton, valence force constants were used. Pilot calculations were made for the in-plane vibrations of s-DMTU by transferring the force constants from NMTU[4] (set 1) and *N*-(methyl)thioacetamide[21,22] (NMTA) (set 2). It was pleasing to note that the agreement between the observed and calculated frequencies for the zero order sets was good indicating the transferability property of the force constants.

The initial values of the valence force constants for a″ modes were obtained from NMTU.[4] The transferred values of the force constants (set 1) were refined for the in-plane vibrations by a least squares procedure[23,24] by keeping some of the force constants such as stretching (CS, CN, NH, and CH), bending (HCH) and repulsion (SCN, NCN) force constants fixed. For the out-of-plane vibrations the force constants were refined by progressive adjustments to obtain a desired agreement between the observed and calculated frequencies. For simplicity, the same force constants

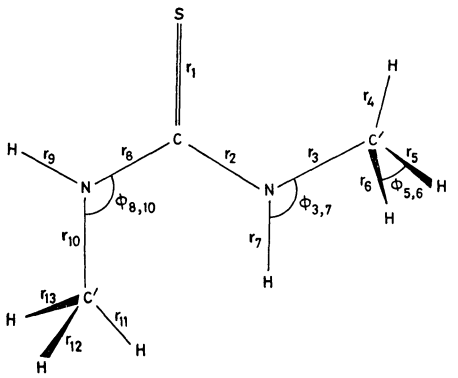

Fig. 1. Molecular structure and internal coordinates of s-DMTU.

were employed for both the *cis* and the *trans*-NH and $-CH_3$ moieties. For this reason the deviation between the observed and calculated frequencies is larger, particulary for the 1188, 1020, and 237 cm^{-1} bands. During the refinement process, it was noted that the potential energy distributions largely remain unaffected.

The computations were performed on an IBM 360/44 digital computer using Fortran programs similar to those of Shimanouchi.[25]

Results and Discussion

Force Field. The previous applications of the normal coordinate procedures for *N*-alkylated thioureas and thioamides have successfully employed the Urey-Bradley force.[1,3-5,7,21,22,26,27] The same has been utilized in the present study. The final values of the force constants are listed in Table 1. The values of the force constants seem reasonable.

The characteristic C=S and C–N stretching constants may now be compared. The C=S stretching constant of s-DMTU (2.65 mdyn/Å) is somewhat lower compared to that of thioacetamide (TA)[26,27] and TCH[9] (3.45 mdyn/Å). The C–N stretching constant of s-DMTU (5.45 mdyn/Å) is closer to that of TCH[9] and NMTU[4] (5.35 mdyn/Å) and *N*-(alkyl)thioamides[21,27] (5.50—5.75 mdyn/Å). The lower C=S and C–N stretching constants of s-DMTU compared to those of TA seem reasonable in relation to their π bond orders. The π bond orders of the C=S group in TA and s-DMTU are 0.637 and 0.514, respectively, while that of C–N bond is 0.585 and 0.550, respectively, as obtained by the CNDO/2 method.[28]

Vibrational Assignments. In Table 3, the results of the present investigation given in Table 2 are compared with the earlier assignments for s-DMTU and also for s-DMU. A satisfactory interpretation of all the frequencies is made by referring to the band shifts on *N*-deuteration and *S*-methylation and the characteristic group frequencies of related thioamides and thioureas.

In-plane Thioureide Group Vibrations. NH and CN Vibrations: The infrared spectrum of s-DMTU in the solid phase exhibits a broad band centred at 3005 cm^{-1}, which could easily be assigned to in- and out-of-phase vibrations of the NH group. The spectrum in $CHCl_3$ at different concentrations gives a strong sharp peak at 3450 cm^{-1} and a broad medium band centered at 3335 cm^{-1}. The intensity of the sharp peak increases and that of the broad band decreases with dilution, indicating the existence of strong hydrogen bonding in the solid state. On *N*-deuteration this broad band is replaced by the new absorptions at 2440 and 2420 cm^{-1}.

According to the normal coordinate calculations, the band at 1560 cm^{-1} is attributable to thioamide III band (B band of Jensen and Nielsen)[29] of the secondary thioamide group. It is slightly coupled with NH bending mode. The analogous band in NMTU[4] (1567 cm^{-1}) and TCH[9] (1547 cm^{-1}) is found in the same region. The potential energy distribution reveals that the 1506 cm^{-1} band could be attributed to a mixed mode of NH bending and C–N stretching. The assignment for the C–N stretching bands may be substantiated by the spectrum of the *S*-methyl derivative. On *S*-methylation, the 1560 cm^{-1} band of s-DMTU shows a larger shift and is found at 1610 cm^{-1} while 1506 cm^{-1} band is found around 1520 cm^{-1}.

The assignment of NH bending vibrations differs from the previous ones.[7,10] Alternate assignments for the NH bending mode were probed through the force field calculations. The assignments described below seemed acceptable.

The potential energy distributions (PEDs) reveal that the *trans*-NH bending mode contributes predominantly (51%) to the 1355 cm^{-1} band which disappears on *N*-deuteration. A new strong band is noted at 936 cm^{-1} in the spectrum of s-DMTU-d_2 as is to be expected consequent to the mass change on replacement of H by D. This assignment of NH bending is in good agreement with that of s-DMU[8] (1328 cm^{-1}), TCH[9] (1333 cm^{-1}) and somewhat higher than in NMTU[4] (1302 cm^{-1}). The other NH bending vibration *cis* to the thiocarbonyl group is coupled mainly with C–N stretching and contributes nearly equally ($\approx$36%) to the bands at 1506 cm^{-1} and a doublet at 1287 and 1260 cm^{-1}.

C=S Stretching: Of particular interest in the spectrum of s-DMTU is the assignment of the C=S stretching (Thioamide I band). Jensen and Nielsen[29] have qualitatively assigned for s-DMTU by comparison with its selenium analogue (s-DMSU), a band at 637 cm^{-1} to C=S stretching. However, the difference in frequency between s-DMTU and s-DMSU (605 cm^{-1}) is rather small (32 cm^{-1}).

According to the potential energy distribution the C=S stretching coordinate contributes substantially ($\approx$40%) to the 725 cm^{-1} absorption. The C=S stretching also contributes significantly ($\approx$20%) to the low frequency bands at 550 and 445 cm^{-1} and to a lesser extent to the high frequency bands at 1020 and 1274 cm^{-1}. Hence the 725 cm^{-1} band may qualitatively be assigned to the C=S stretching vibration. This assignment is in agreement with Ritchie *et al.*[10] and is concordant with the Raman data.[10,13] Further evidence for the assignment of C=S mode comes from the infrared spectrum of the *S*-methyl derivative. The 725 cm^{-1} band shifts to 708 cm^{-1} with the decreasing C=S bond

Table 1. Force constants for s-DMTU

Urey-Bradley constants (mdyn/Å)								
K	Initial	Final	H	Initial	Final	F	Initial	Final
CS	3.40	2.650	NCS	0.24	0.238	NCS	1.02	1.050
CN	5.50	5.450	NCN	0.50	0.693	NCN	0.60	0.550
C'N	3.45	4.124	CNH	0.20	0.265	CNH	0.45	0.432
NH	5.20	5.600	HNC'	0.12	0.203	HNC'	0.60	0.366
CH	4.40	4.250	CNC	0.25	0.264	CNC	0.25	0.207
			NCH	0.28	0.268	NCH	0.55	0.595
			HCH	0.41	0.410	HCH	0.05	0.057
k (Intramolecular tension) (mdyn Å)								
CH_3	−0.040	−0.042						
Valence constants (mdyn Å)								
$f(\pi^cNH)$	0.062	$f(\pi^tNH)$	0.057	$f(\tau^cCN)$	0.105	$f(\tau^tCN)$	0.098	
$f(\pi CS)$	0.0935	$f(\pi^tCH_3)$	0.0065	$f(\tau^cCH_3)$	0.0070			

Abbreviations: π, τ, C', c, and t as in Table 2.

Table 2. Observed and calculated frequencies (cm^{-1}) and assignments of s-DMTU-d_0 and -d_2

s-DMTU-d_2		s-DMTU-d_0		Assignment (PED, %)
Obsd	Calcd	Obsd	Calcd	
A' Species				
2420	2424	3305	3311	$\nu^tNH(63)$, $\nu^cNH(36)$
2420	2419	3305	3309	$\nu^cNH(63)$, $\nu^tNH(36)$
2938	2923	2940	2923	$\nu_a{}^cCH_3(76)$, $\nu_a{}^tCH_3(24)$
2938	2923	2940	2923	$\nu_a{}^tCH_3(76)$, $\nu_a{}^cCH_3(24)$
2860	2857	2850	2857	$\nu_s{}^cCH_3(73)$, $\nu_s{}^tCH_3(27)$
2860	2857	2850	2857	$\nu_s{}^tCH_3(73)$, $\nu_s{}^cCH_3(27)$
1540	1535	1560	1561	$\nu CN(53)$, $\delta^tNH(18)$
1475	1463	1506	1505	$\delta^cNH(34)$, $\nu CN(28)$
1460	1444	1455	1450	$\delta_a{}^tCH_3(76)$, $r^tCH_3(17)$
1445	1425	1445	1445	$\delta_a{}^cCH_3(74)$, $r^cCH_3(13)$
1412	1412	1418	1412	$\delta_s{}^cCH_3(48)$, $\delta_s{}^tCH_3(41)$
1412	1407	1418	1412	$\delta_s{}^tCH_3(48)$, $\delta_s{}^cCH_3(41)$
936	926	1355	1367	$\delta^tNH(47)$, $\nu CN(27)$
936	922	1287,1260	1259	$\delta^cNH(40)$, $\nu CN(21)$, $\delta NCN(11)$
1221	1248	1188	1170	$\nu^cNC'(58)$, $\delta^tNH(13)$
1152	1142	1148	1143	$\nu^tNC'(44)$, $r^tCH_3(16)$, $r^cCH_3(12)$
1068	1082	1035	1046	$r^tCH_3(53)$, $\nu^tNC'(12)$, $\delta_a{}^cCH_3(12)$
1030	1071	1020	1039	$r^cCH_3(53)$, $\delta_a{}^cCH_3(13)$, $\nu C{=}S(11)$
712	709	725	736	$\nu C{=}S(37)$, $\nu CN(25)$, $\delta NCN(11)$
550	527	550	537	$\nu C{=}S(23)$, $\delta NCS(22)$, $\delta CNC(19)$, $\delta^tNCN(15)$
442	441	445	449	$\delta NCS(36)$, $\nu C{=}S(18)$, $\delta^cCNC(13)$
211	236	211	238	$\delta^cCNC(38)$, $\delta^tCNC(27)$, $\delta NCS(26)$
193	182	193	184	$\delta^tCNC(37)$, $\delta NCN(28)$, $\delta^cCNC(27)$
A'' Species				
2938	2940	2940	2940	$\nu_a{}^cCH_3(99)$
2938	2940	2940	2940	$\nu_a{}^tCH_3(99)$
1445	1453	1455	1453	$\delta_a{}^tCH_3(42)$, $\delta_a{}^cCH_3(40)$
1445	1453	1455	1453	$\delta_a{}^cCH_3(42)$, $\delta_a{}^tCH_3(40)$
1068	1078	1035	1078	$r^tCH_3(53)$, $r^cCH_3(25)$
1068	1076	1035	1076	$r^cCH_3(53)$, $r^tCH_3(25)$
550	537	662	662	$\nu CN(45)$, $\pi^cNH(31)$
485	480	642	645	$\tau CN(47)$, $\pi^tNH(34)$
418	403	445	448	$\pi C{=}S(80)$
193	185	193	189	$\pi^cNH(42)$, $\tau CN(24)$, $\pi^tNH(15)$
150	149	150	150	$\tau^cCH_3(42)$, $\tau^tCH_3(22)$, $\tau CN(17)$
140	141	142	140	$\tau^cCH_3(49)$, $\tau^tCH_3(21)$
130	129	130	130	$\tau^tCH_3(40)$, $\pi^tNH(21)$, $\pi^cNH(17)$

Abbreviation: ν-stretching, δ-bending, r-rocking, π-out-of-plane bending, τ-torsion, s-symmetric, a-asymmetric; c-*cis* and t-*trans*, C' denotes methyl carbon, *cf.* Table 3.

Table 3. Comparison of the vibrational assignments for s-DMTU

Mode	s-DMU Mido *et al.* [a]	Rao *et al.* [b]	s-DMTU Ritchie *et al.* [c]	Present work	Main assignment
In-plane (A')	3360	3282	—	3305	νNH
	2980	—	—	2940	$\nu_a CH_3$
	2930	—	—	2850	$\nu_s CH_3$
	1596	1568	1554	1560	νCN+δNH
	1455	1446	—	1455 1445	$\delta_a CH_3$
	1410	1358	—	1418	$\delta_s CH_3$
	1328	1506	1504	1506	δNH+νCN
	1266	1420	1287	1355	
				1287 1260	δNH+νCN
	1170	1082	1186 1151	1188 1148	νNC'+rCH_3
	1132 1037	1038 851	—	1035 1020	rCH_3+νNC'
	1625	754	722	725	νC=O/νC=S
	672	551	550 220	445 550	δNCO/δNCS
	504 202	446	443 248	550 193	δNCN
	282 202	667	550	211 193	δCNC
Out-of-plane (A'')	—	—	—	2940	$\nu_a CH_3$
	—	—	—	1455	$\delta_a CH_3$
	—	—	—	1035	rCH_3
	—	726	—	662 642	πNH+τCN
	—	416	493	445	πC=S
	—	—	—	193 150	τCN
	—	—	—	140 130	τCH_3

a) Ref. [8]. b) Ref. [7]. c) Ref. [10].

order upon *S*-methylation. The C=S stretching frequency of s-DMTU is thus in the same region as in TA[26] (719 cm^{-1}), TU[1] (736 cm^{-1}), and NMTA[21] (699 cm^{-1}).

Skeletal Bending: The skeletal bending modes occur as highly coupled vibrations. Calculations indicate that NCN bending is highly delocalized and contributes to the frequencies at 193, 445, 550, 725, and 1274 cm^{-1}. In contrast, in s-DMU, NCN bending contributes mainly (46%) to 504 cm^{-1} band and to some extent (22%) to the 202 cm^{-1} frequency.[8] The characteristic NCS bending is also a highly mixed mode and contributes to the bands at 550, 445, and 211 cm^{-1}. The 445 cm^{-1} band could qualitatively be assigned to NCS bending in comparison with the 460 cm^{-1} of TA.[26] The contribution of NCS bending vibration to 550 and 445 cm^{-1} bands is evidenced by the shifting of these bands to slightly higher wave numbers (567 and 452 cm^{-1}) in the infrared spectrum of the *S*-methyl derivative.

According to the coordinate treatment, the 211 and 193 cm^{-1} bands correspond to CNC bending vibrations. This assignment compares reasonably with that of s-DMU[8] assigned at 282 and 202 cm^{-1}.

Out-of-plane Vibrations. There are five a'' modes for the planar skeleton. The present study indicates that the 662 and 642 cm^{-1} bands have their origin in the N–H vibrations as inferred by deuteration studies and normal coordinate analysis. On deuteration these bands disappear and the intensity of the 445 cm^{-1} band of s-DMTU increase in the spectrum of s-DMTU-d_2 indicating overlapping of ND out-of-plane bending with the 445 cm^{-1} fundamental. The present assignment for NH bending is at a lower frequency than the analogous band of TCH (768, 579 cm^{-1}).

The out-of-plane C=S bending is assigned to the 445 cm^{-1} band in the infrared (at 450 cm^{-1} in the Raman) in comparison with that in NMTU (400 cm^{-1}). The two CN torsional vibrations are strongly coupled with out-of-plane NH bending modes and contribute to low frequencies at 193, 150, and 142 cm^{-1}. These assignments are comparable with those in TMTU[6] at 144 and 127 cm^{-1} and in TCH[9] at 194 and 140 cm^{-1}.

Methyl Group Vibrations. The stretching and bending vibrations of the CH_3 group are easily assigned as shown in Table 2. The CH_3 rocking vibrations occur as coupled vibrations. They contribute principally to the bands at 1035 and 1020 cm^{-1} coupled with C'N stretching vibrations. The frequencies of the rocking vibrations are in the same region as observed for

NMTU[4] at 980 cm^{-1}, NMTA[21] at 1023 cm^{-1} and TMTU[6] at 1061 and 1035 cm^{-1}. The band at 1035 cm^{-1} may be attributed to both the out-of-plane CH_3 rocking (wagging) vibrations overlapping with an in-plane fundamental. The analogous rocking vibrations are observed for u-DMTU at 1068 and 1035 cm^{-1}, and in NMTU and TMTU near 1040 cm^{-1}.

The calculations suggest that the CH_3 torsional vibrations could be assigned to the bands near 140 and 130 cm^{-1}. The 144 and 127 cm^{-1} bands of TMTU are the corresponding ones. The CH_3 torsion is found near 130 cm^{-1} in NMTU[4] and *N,N*-dimethylselenoformamide.[30]

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