Infrared Spectra and Normal Vibrations of *N,N*-Dimethylformamide and *N,N*-Dimethylthioformamide*

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The infrared spectra of *N,N*-dimethylformamide (DMF) and *N,N*-dimethylthioformamide (DMTF) have been investigated in the range 4000—250 cm^{-1}. Assignment of the frequencies of DMF has been made on the basis of normal coordinate analysis for DMF, DMF-^{15}N, and DMF-d_7 using Urey-Bradly, modified Urey-Bradley, and symmetrized valence force fields. Calculations have been extended to *N,N*-dimethylthioformamide and *N,N*-dimethylselenoformamide, using the Urey-Bradley and symmetrized valence force fields. The assignments for DMF from the modified Urey-Bradley field are found to be more satisfactory. The frequency shifts on isotopic substitution and on complexation have been explained. The results of the calculations are discussed in comparison with other related molecules.

The infrared spectra of amides have been subjected to many studies.[1-5] Detailed assignments are available in literatures for primary and secondary amides.[1-4,6-8] In these amides, the characteristic infrared frequencies are due to highly coupled vibrations and the N–H bending mode is mixed extensively with the other vibrations. However, in the case of tertiary amides, the C–N stretching mode appears in the region of C–H bending vibration, rendering its identification difficult.

The simplest tertiary amide is *N,N*-dimethylformamide (DMF). While there has been no difficulty in assigning some of its frequencies, a satisfactory and complete assignment of the infrared spectrum has not been possible. The valence bond approach to assign a few important bands from the frequency changes in metal complexes of DMF has not been helpful. The different earlier assignments for a few important bands have been summarized by Randall *et al.*[9]

Kaufman and Leroy[10] have carried out a force constant calculation for DMF and made assignments which follow largely those of *N*-methylformamide by Suzuki[2] and those of DMF by Jones.[3] Chalapathi and Ramaiah[11] have made a normal vibration calculation for the DMF skeleton. Their assignments comply generally to the earlier assignments. The different assignments[9-11] for DMF have not been substantiated and doubts regarding the assignment of some of the bands still exist. For example, the band at 1395 cm^{-1} in DMF has been assigned to C–H bending vibration, which appears to be incorrect, since the same band is present in DMF-d_1.[12] Moreover, the frequency shifts are now available from the spectrum of DMF-^{15}N which could be used to test the validity of a potential field employed. This tempted us to undertake a fresh normal coordinate treatment to make a reasonable and complete assignment for DMF. As the assignments are known to be somewhat sensitive to the force fields, the three commonly employed potential fields were tried. The study includes related *N,N*-dimethylthioformamide (DMTF) and *N,N*-dimethylselenoformamide (DMSeF) for understanding the nature of the vibrations in the simplest thioamides and selenoamides.

Experimental

Dimethylformamide used was a product of Riedel De Haen AG which was redistilled at reduced pressure, after keeping over KOH pellets for four days. Dimethylthioformamide was obtained through the courtesy of Prof. W. Walter, Institute of Organic Chemistry, Hamburg.

The infrared spectra of DMF and DMTF as thin films were recorded on a Carl-Zeiss UR 10 Spectrophotometer in the range 4000—400 cm^{-1} and on a Perkin-Elmer 521 Grating Spectrophotometer in the range 400—250 cm^{-1}. The spectra in the range 400—1800 cm^{-1} are given in Fig. 1. The infrared spectra of DMF-d_7 and DMF-^{15}N were kindly supplied by Dr. T. H. Siddall, III,[13] Savannah River Laboratory, E. I. du Pont de Nemours & Co., Aiken, South Carolina and Dr. J. J. Zuckerman,[9] Department of Chemistry, State University of New York at Albany, respectively.

Normal Coordinate Treatment

The vibrational problem was set up in internal coordinates, using GF matrix method.[14] The secular

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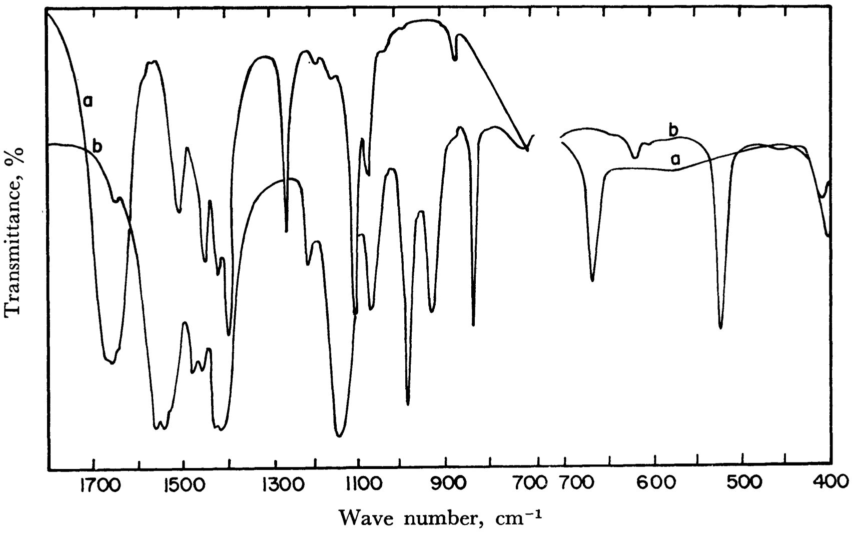

Fig. 1. Infrared spectra of (a) DMF and (b) DMTF.

equation was solved using Miyazawa's method[15,16] on a National Elliott 803 computer. The least squares adjustment of the frequencies has not been made because of the small computer at hand. The high frequency C–H stretching modes were split off from the lower vibrations for the same reason.

Dimethylformamide belongs to the point group C_S and its 30 fundamental vibrations are split into $19A'$ and $11A''$ vibrations. The calculations have been made for the A' vibrations only, since the assignment of frequencies in question belong to this species. The internal coordinates are defined in Fig. 2 and the symmetry coordinates are given in Table 1.

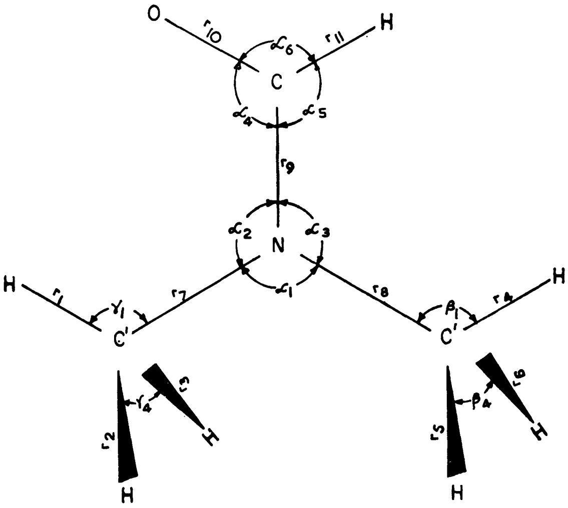

Fig. 2. Internal coordinates for DMF.

The structural parameters of DMF are taken from the electron diffraction data,[17] except for the angles around carbonyl carbon which are from the microwave data of formamide.[18] The C=S bond length is taken as in thioformamide[2] while C=Se distance is from the covalent radii. The other parameters for DMTF and DMSeF are the same as those of DMF. The structural parameters are listed in Table 2.

TABLE 1. SYMMETRY COORDINATES

Symmetry coordinate	Description[a]
$S_1=(2\Delta r_1-\Delta r_2-\Delta r_3+2\Delta r_4-\Delta r_5-\Delta r_6)/\sqrt{12}$	$\nu_a(CH_3)$
$S_2=(2\Delta r_1-\Delta r_2-\Delta r_3-2\Delta r_4+\Delta r_5+\Delta r_6)/\sqrt{12}$	$\nu_a(CH_3)$
$S_3=(\Delta r_1+\Delta r_2+\Delta r_3+\Delta r_4+\Delta r_5+\Delta r_6)/\sqrt{6}$	$\nu_s(CH_3)$
$S_4=(\Delta r_1+\Delta r_2+\Delta r_3-\Delta r_4-\Delta r_5-\Delta r_6)/\sqrt{6}$	$\nu_s(CH_3)$
$S_5=\Delta r_{11}$	$\nu(CH)$
$S_6=(\Delta r_7+\Delta r_8)/\sqrt{2}$	$\nu_s(C'N)$
$S_7=(\Delta r_7-\Delta r_8)/\sqrt{2}$	$\nu_a(C'N)$
$S_8=\Delta r_9$	$\nu(CN)$
$S_9=\Delta r_{10}$	$\nu(CO)$
$S_{10}=(2\Delta\alpha_1-\Delta\alpha_2-\Delta\alpha_3)/\sqrt{6}$	$\delta(C'NC')$
$S_{11}=(\Delta\alpha_2-\Delta\alpha_3)/\sqrt{2}$	$r(C'NC')$
$S_{12}=(2\Delta\alpha_4-\Delta\alpha_5-\Delta\alpha_6)/\sqrt{6}$	$\delta(OCN)$
$S_{13}=(\Delta\alpha_5-\Delta\alpha_6)/\sqrt{2}$	$\delta(CH)$
$S_{14}=(2\Delta\gamma_4-\Delta\gamma_5-\Delta\gamma_6+2\Delta\beta_4-\Delta\beta_5-\Delta\beta_6)/\sqrt{12}$	$\delta_a(CH_3)$
$S_{15}=(2\Delta\gamma_4-\Delta\gamma_5-\Delta\gamma_6-2\Delta\beta_4+\Delta\beta_5+\Delta\beta_6)/\sqrt{12}$	$\delta_a(CH_3)$
$S_{16}=(-\Delta\gamma_1-\Delta\gamma_2-\Delta\gamma_3+\Delta\gamma_4+\Delta\gamma_5+\Delta\gamma_6$ $-\Delta\beta_1-\Delta\beta_2-\Delta\beta_3+\Delta\beta_4+\Delta\beta_5+\Delta\beta_6)/\sqrt{12}$	$\delta_s(CH_3)$
$S_{17}=(-\Delta\gamma_1-\Delta\gamma_2-\Delta\gamma_3+\Delta\gamma_4+\Delta\gamma_5+\Delta\gamma_6$ $+\Delta\beta_1+\Delta\beta_2+\Delta\beta_3-\Delta\beta_4-\Delta\beta_5-\Delta\beta_6)/\sqrt{12}$	$\delta_s(CH_3)$
$S_{18}=(2\Delta\gamma_1-\Delta\gamma_2-\Delta\gamma_3+2\Delta\beta_1-\Delta\beta_2-\Delta\beta_3)/\sqrt{12}$	$r(CH_3)$
$S_{19}=(2\Delta\gamma_1-\Delta\gamma_2-\Delta\gamma_3-2\Delta\beta_1+\Delta\beta_2+\Delta\beta_3)/\sqrt{12}$	$r(CH_3)$
$S_{20}=(\Delta\alpha_1+\Delta\alpha_2+\Delta\alpha_3)/\sqrt{3}$	Redundant
$S_{21}=(\Delta\alpha_4+\Delta\alpha_5+\Delta\alpha_6)/\sqrt{3}$	Redundant
$S_{22}=(\Delta\gamma_1+\Delta\gamma_2+\Delta\gamma_3+\Delta\gamma_4+\Delta\gamma_5+\Delta\gamma_6$ $+\Delta\beta_1+\Delta\beta_2+\Delta\beta_3+\Delta\beta_4+\Delta\beta_5+\Delta\beta_6)/\sqrt{12}$	Redundant

a) ν, δ, r, a, and s mean stretching, bending, rocking, asymmetric, and symmetric, respectively.

The final sets of force constants, for DMF and DMTF, obtained after several trials, are given in Tables 3 and

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Table 2. Structural parameters of DMF, DMTF, and DMSeF

Bond length		Bond angle	
C–H	1.08 Å	HC′N	109°28′
C′–N	1.45	C′NC′	117°30′
C–N	1.34	C′NC	121°15′
C=O	1.22	NCO	123°
C=S	1.713	HCO	
C=Se	1.91		

4, respectively. The observed and calculated frequencies for DMF, DMF-^{15}N and DMF-d_7 along with their assignments from the modified Urey-Bradley field (MUBF) are given in Table 5. The frequencies for DMTF and their assignments from Urey-Bradley field (UBF) are given in Table 6. Finally, the present assignments for DMF are compared with the previous assignments in Table 7.

Results and Discussion

Dimethylformamide. *Lower Vibrations*: The lowest frequency in the spectrum at 319 cm^{-1} is assigned to C′NC′ rocking vibration, instead of a band at 350 cm^{-1} as assigned by Kaufman and Leroy.[10)] Katon *et al.*[4)] favour the band near 350 cm^{-1} to a similar wagging mode in amides. The 350 cm^{-1} band may, therefore, be assigned to C′NC′ wagging vibration. The bands at 405 and 660 cm^{-1} need no comment since their

Table 3. Force constants for DMF (md/Å, md/rad, md Å/rad^2)

	Stretching		Bending		Repulsive		Interactions[a)]	
MUBF	*K*(C′–N)	4.30	*H*(HCH)	0.512				
	K(C–N)	5.66	*H*(HC′N)	0.787				
	K(C=O)	8.85	*H*(C′NC)	0.734	*F*(C′C)	0.6269	C′N with HC′N	0.4264
			H(C′NC′)	0.526	*F*(C′C′)	0.26	HC′N with H$_0$C′N	−0.017
			H(NCO)	0.955	*F*(NO)	1.154	H$_0$C′N with H$_0$C′N	
			H(NCH)	0.268	*F*(NH)	0.72	C′NC with HC′N	0.2078
			H(OCH)	0.270	*F*(OH)	0.92	C′NC with H$_0$C′N	0.06

	Stretching		Bending		Repulsive		Intramolecular tension	
UBF	*K*(C′–N)	3.24	*H*(HCH)	0.502	*F*(HH)	0.05	*k*	−0.04
	K(C–N)	6.11	*H*(HC′N)	0.439	*F*(HC′N)	0.52		
	K(C=O)	8.565	*H*(C′NC)	0.905	*F*(C′C)	0.42		
			H(C′NC′)	0.505	*F*(C′C′)	0.30		
			H(NCO)	0.726	*F*(NO)	1.50		
			H(NCH)	0.253	*F*(NH)	0.72		
			H(OCH)	0.257	*F*(OH)	0.92		
SVF	F_{66}	5.35	F_{1212}	1.38	F_{1818}	0.85	F_{89}	1.20
	F_{77}	4.58	F_{1313}	0.63	F_{1919}		F_{812}	0.45
	F_{88}	6.40	F_{1414}	0.52	F_{616}	−0.35	F_{813}	0.25
	F_{99}	10.85	F_{1515}	0.51	F_{711}	0.42	F_{912}	0.40
	F_{1010}	0.90	F_{1616}	0.59	F_{717}	−0.35	F_{913}	−0.25
	F_{1111}	1.06	F_{1717}					

a) H and H$_0$ denote hydrogen atom lying in and out-of-plane of the molecule.

Table 4. Force constants for DMTF (md/Å, md/rad, md Å/rad^2)

	Stretching		Bending		Repulsive		Intramolecular tension	
UBF	*K*(C′–N)	3.04	*H*(HCH)	0.478	*F*(HH)	0.06	*k*	−0.05
	K(C–N)	6.20	*H*(HC′N)	0.493	*F*(HC′N)	0.50		
	K(C=S)	4.18	*H*(C′NC)	0.777	*F*(C′C)	0.46		
			H(C′NC′)	0.746	*F*(C′C′)	0.30		
			H(NCS)	0.404	*F*(NS)	0.92		
			H(NCH)	0.278	*F*(NH)	0.65		
			H(SCH)	0.263	*F*(SH)	0.60		
SVF	F_{66}	5.58	F_{1212}	0.86	F_{1818}	0.89	F_{89}	0.65
	F_{77}	4.44	F_{1313}	0.61	F_{1919}	0.87	F_{812}	0.25
	F_{88}	6.45	F_{1414}	0.51	F_{616}	−0.30	F_{813}	0.20
	F_{99}	5.05	F_{1515}		F_{711}	0.41	F_{912}	0.30
	F_{1010}	1.05	F_{1616}	0.58	F_{717}	−0.30	F_{913}	−0.25
	F_{1111}	1.00	F_{1717}					

Table 5. Calculated and observed frequencies (cm^{-1}) and potential energy distribution for DMF, DMF^{15}N, and DMF-d_7

	Calculated			Observed[a]	Approx. PED. (MUBF)
	MUBF	UBF	SVF		
DMF	318	319	318	319 m	$r(C'NC')+0.52\delta(OCN)$
	405	405	406	405 m	$\delta(C'NC')$
	660	662	669	660 s	$\delta(OCN)+0.54\nu_s(C'N)+0.42\nu_a(C'N)+0.36r(C'NC')$
	872	856	855	870 m	$\nu_s(C'N)$
	1059	1017	1069	1067 m	$r(CH_3)+0.38\nu_a(C'N)$
	1085	1046	1095	1099 vs	$r(CH_3)$
	1264	1293	1279	1268 s	$\nu_a(C'N)$
	1376	1397	1397	1395 vs	$\delta_s(CH_3)+0.67\nu(CN)+0.34\nu_s(C'N)$
	1409	1414	1406	(1410)	$\delta(CH)$
	1430	1418	1409	1410 s	$\delta_s(CH_3)$
	1454	1432	1435	1450 m	$\delta_a(CH_3)+0.61\delta_s(CH_3)$
	1460	1473	1465	1460 w	$\delta_a(CH_3)$
	1493	1504	1508	1512 m	$\delta_s(CH_3)+0.91\delta_a(CH_3)+0.76\nu(CN)+0.74r(CH_3)$
	1690	1683	1677	1685 vs	$\nu(CO)+0.41\nu(CN)+0.31\delta(CH)$
DMF-^{15}N	317	318	317	[b]	$r(C'NC')+0.51\delta(OCN)$
	404	406	405	[b]	$\delta(C'NC')$
	659	661	668	653 w	$\delta(OCN)+0.51\nu_s(C'N)+0.41\nu_a(C'N)+0.37r(C'NC')$
	870	854	854	862 w	$\nu_s(C'N)$
	1056	1016	1063	1059 w	$r(CH_3)+0.47\nu_a(C'N)$
	1084	1046	1094	1081 vs	$r(CH_3)$
	1239	1267	1258	1234 m	$\nu_a(C'N)$
	1362	1396	1395	1369 s	$\nu(CN)+0.95\delta_s(CH_3)+0.44\nu_s(C'N)$
	1408	1413	1399	1395 vw	$\delta(CH)$
	1430	1416	1409	1404 w	$\delta_s(CH_3)$
	1452	1419	1426	1432 m	$\delta_s(CH_3)+0.96\delta_a(CH_3)$
	1460	1472	1464	1451 w	$\delta_a(CH_3)$
	1481	1493	1497	1493 m	$\delta_a(CH_3)+0.69\delta_s(CH_3)+0.53r(CH_3)+0.38\nu(CN)$
	1686	1676	1675	1684 vs	$\nu(CO)+0.37\nu(CN)+0.3\delta(CH)$
DMF-d$_7$	293	291	290	288 vs	$r(C'NC')+0.49\delta(OCN)+0.3\delta(C'NC')$
	352	350	351	344 m	$\delta(C'NC')$
	623	615	618	619 vs	$\delta(OCN)+0.57\nu_s(C'N)+0.37\nu_a(C'N)+0.3r(C'NC')$
	771	747	760	765 s	$\nu_s(C'N)+0.7r(CH_3)$
	823	793	845	834 s	$r(CH_3)$
	862	840	865	890 vs	$r(CH_3)+0.3\delta(CH)$
	1045	1044	1042	1035 s	$\delta_a(CH_3)$
	1047	1050	1053	1046 s	$\delta_a(CH_3)$
	1060	1055	1058	1052 s, sh	$\delta_s(CH_3)$
	1074	1076	1076	1068 s, sh	$\delta(CH)+0.54\delta_s(CH_3)$
	1107	1127	1119	1120 s	$\delta_s(CH_3)+0.32\nu_s(C'N)$
	1263	1298	1264	1258 vs	$\nu_a(C'N)$
	1402	1437	1428	1385 vs, b	$\nu(CN)$
	1670	1666	1654	1645 vs, b	$\nu(CO)+0.42\nu(CN)$

a) s, m, w, v, b, and sh mean strong, medium, weak, very, broad, and shoulder, respectively.
b) spectrum in this region was not obtained.

assignments are undoubted.

Methyl Rocking Vibrations: The bands at 1067 and 1099 cm^{-1} are assigned to methyl rocking vibrations of the *A'* type while the methyl rocking mode of the *A''* type is observed as a weak band at 1150 cm^{-1}. The 1099 cm^{-1} band in DMF increases by about 25 cm^{-1} in metal complexes and was assigned to C–N stretching mode since the double bond character of C–N is expected in increase on theoretical grounds with the decreasing bond order of C=O in metal complexes.[9] However, that this correlation is misleading may be judged from: (a) the infrared spectra of compounds containing gem dimethyl groups [includes –N(CH$_3$)$_2$] show strong bands in the region 1000—1200 cm^{-1} for CH$_3$ rocking modes,[19–23] and hence the assignment of frequencies at 1067, 1099, and 1150 cm^{-1}

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TABLE 6. CALCULATED AND OBSERVED FREQUENCIES (cm^{-1}) AND POTENTIAL ENERGY DISTRIBUTION FOR DMTF

Calcd		Obsd	Approx. PED (UBF), %
UBF	SVF		
220	215	[a]	δ(SCN) 58, r(C′NC′) 37
407	406	405 m	δ(C′NC′) 65, r(C′NC′) 16, ν(CS) 8
527	529	521 s	δ(C′NC′) 23, δ(SCN) 21, r(C′NC′) 21, ν(CS) 12, ν_s(C′N) 9, ν_a(C′N) 9
816	810	828 s	ν_s(C′N) 68, ν(CN) 8, δ(SCN) 9
974	975	975 vs	ν(CS) 50, r(CH$_3$) 17, ν_s(C′N) 10
1024	1064	1058 s	r(CH$_3$) 64, ν_a(C′N) 19, δ_a(CH$_3$) 14
1091	1123	1140 vs	r(CH$_3$) 49, ν(CS) 20, δ_a(CH$_3$) 12, ν(CN) 11
1238	1236	1212 m	ν_a(C′N) 45, δ(CH) 15, r(C′NC′) 14, r(CH$_3$) 11
1392	1395	1405 vs	δ(CH) 39, δ_a(CH$_3$) 21, ν(CN) 12
1417	1406	1410 vs, sh	δ_s(CH$_3$) 95
1421	1424	1420 vs	δ_s(CH$_3$) 92
1449	1455	1450 m	δ_a(CH$_3$) 64, δ(CH) 16
1464	1469	1472 m	δ_a(CH$_3$) 62, r(CH$_3$) 17, δ(CH) 11
1561	1561	1560 vs	ν(CN) 53, δ(CH) 13, r(CH$_3$) 12

a) Spectrum was not scanned in this region.

to CH$_3$ rocking vibrations is reasonable, (b) rocking frequencies are sensitive and are known to shift on complex formation[22]; thus the frequency rise of the CH$_3$ rocking mode in DMF metal complexes is not unexpected, and (c) the 1099 cm^{-1} band does not show any change in the infrared spectrum[9] of DMF-^{15}N, thus ruling out any major C–N stretching contribution in the 1099 cm^{-1} band. Only about 10% C–N character is indicated by the calculation. The assignment of 1099 cm^{-1} to methyl rocking mode is in accord with these facts.

C=O *and* C′–N *Stretching Vibrations*: There is complete agreement over the assignment of the bands at 1685, 1268, and 870 cm^{-1} to C=O stretching, C′–N asymmetric and symmetric stretching vibrations, respectively. The carbonyl band has contributions from C–N stretching and C–H bending modes, as also expected by others.[10,11] From the band shapes of the vapor phase spectrum, Jones[3] has supported the assignment of C′–N symmetric and asymmetric stretching, OCN bending and CH$_3$ rocking vibrations and these agree with the present assignments.

C–N *Stretching Vibration*: The weak to medium band at 1512 cm^{-1} is a highly coupled vibration and has a complex character. This band is due to a CH$_3$ deformation vibration with contributions from CH$_3$ rocking and C–N stretching vibrations. The mixing of CH$_3$ deformation modes with skeletal vibrations has been found in other similar molecules containing gem dimethyl groups.[20,23] The 1512 cm^{-1} band of DMF is absent in diethylformamide (DEF).[5] It could, therefore, be expected that the coupling of CH$_3$ deformation vibrations with C–N stretching mode, present in DMF, does not occur in DEF. The band assignable to C–N stretching motion in DEF appears in the region 1420—1370 cm^{-1}.

The 1512 cm^{-1} band hardly shifts by 5 cm^{-1} in metal complexes. In the spectrum of DMF-^{15}N, the 1512 cm^{-1} band is lowered by 7 cm^{-1}, while the calculated shifts are -11 to -12 cm^{-1}.

C–H *Bending and* CH$_3$ *Deformation Vibrations*: The assignments in the region 1395—1450 cm^{-1} were found to be very sensitive to the force fields employed. In the UBF, the 1397, 1414, and 1418 cm^{-1} and in the symmetrized valence field (SVF), the 1397, 1409, and 1406 cm^{-1} bands have approximately the same assignments as the bands at 1409, 1430, and 1376 cm^{-1} in the MUBF (Table 5).

The MUBF calculations indicate that the 1376 and 1430 cm^{-1} bands are due to CH$_3$ symmetric deformation vibrations, and the band at 1409 cm^{-1} to C–H

TABLE 7. A COMPARISON OF THE ASSIGNMENTS FOR DMF IN THE RANGE 300—1700 cm^{-1} [a]

Obsd, cm^{-1}	J[3]	KL[10]	RYZ[9]	CR[11]	Present work (PED, %)
319				r(C′NC′)	r(C′NC′) 56, δ(OCN) 29, δ(C′NC′) 11
350		δ(C′NC)		τ(CN)	r(C′NC′) ⊥
405		δ(C′NC′)		δ(C′NC′)	δ(C′NC′) 78, r(C′NC′) 14
660	δ(OCN)	δ(OCN)		δ(OCN)	δ(OCN) 36, ν_s(C′N) 19, ν_a(C′N) 15, r(C′NC′) 13
870	ν_s(C′N)	ν_s(C′N)		ν_s(C′N)	ν_s(C′N) 65, δ(OCN) 14, ν_a(C′N) 10
1067		r(CH$_3$) ⊥		δ(CH) ⊥	r(CH$_3$) 66, ν_a(C′N) 16
1099	r(CH$_3$)	r(CH$_3$)	δ(CH)	r(CH$_3$)	r(CH$_3$) 75, ν(CN) 9
1150	r(CH$_3$) ⊥			r(CH$_3$) ⊥	r(CH$_3$) ⊥
1268	ν_a(C′N)	ν_a(C′N)	ν_a(C′N)	ν_a(C′N)	ν_a(C′N) 49, r(C′NC′) 12
1395	δ(CH)	δ(CH)ν(CO)ν(CN)	ν(CN)	δ(CH)	δ_s(CH$_3$) 35, ν(CN) 24, ν_s(C′N) 12
1410	δ_s(CH$_3$)	δ_s(CH$_3$)		δ_s(CH$_3$)	δ(CH) 64, ν(CO) 15, δ_s(CH$_3$) 12
1410[b]					δ_s(CH$_3$) 84, δ(CH) 9
1450					δ_a(CH$_3$) 56, δ_s(CH$_3$) 34
1460	δ_a(CH$_3$)	δ_a(CH$_3$)		δ_a(CH$_3$)	δ_a(CH$_3$) 82, r(CH$_3$) 13
1512	ν(CN)	ν(CN)ν(CO)δ(CH)		ν(CN)	δ_s(CH$_3$) 23, δ_a(CH$_3$) 21, ν(CN) 18, r(CH$_3$) 17
1685	ν(CO)	ν(CO)ν(CN)δ(CH)	ν(CO)	ν(CO)	ν(CO) 55, ν(CN) 23, δ(CH) 17

a) See footnote to Table 1. τ: Torsion, ⊥: Out-of-plane

b) Not resolved.

bending vibration. The CH_3 asymmetric deformation vibrations are easily located at 1450 and 1460 cm^{-1}.

The 1395 cm^{-1} band is a coupled vibration with major contributions from CH_3 deformation (~35%) and C–N stretching (~24%) modes. It is lowered by 20 to 40 cm^{-1} in metal complexes and this shift may be understood from the major components of the band. It is also known that the CH_3 symmetric deformation vibration is more sensitive to the atom adjacent to the methyl group than the asymmetric vibration.[22)]

The 1395 cm^{-1} band in DMF was observed to shift by −13 cm^{-1} in the spectrum[9)] of DMF-^{15}N, which is in good agreement with the calculated value of −14 cm^{-1} in the MUBF. It should be noted that the calculated frequencies for DMF-^{15}N in the UBF and SVF indicate no shift for 1395 cm^{-1} band, which is contradictory to the experimental data. On the other hand, the calculations showed shifts for 1432 cm^{-1} frequency in the UBF and 1406 and 1435 cm^{-1} frequencies in the SVF, which is again contradictory to the observed data, since these bands remain unaffected in the infrared spectrum of DMF-^{15}N. This piece of evidence suggests that the assignments from the MUBF are to be preferred.

Some of the earlier investigators had favoured the assignment of the 1395 cm^{-1} band to C–H bending mode.[3,10,11)] That this band is not due to C–H bending vibration also finds support from the spectrum of DMF-d_1.[24)] Castelli and Cragle[12)] have recorded the infrared spectra of DMF and DMF-d_1 as liquids. It is found that (a) a shoulder at 1400 cm^{-1} in DMF (corresponding to 1410 cm^{-1} of the present work) is absent in the spectrum of DMF-d_1, and is observed at ~1010 cm^{-1} as expected with the replacement of hydrogen by deuterium, indicating that this band can be assigned to C–H bending vibration, and (b) the band at 1380 cm^{-1} (this work, 1395 cm^{-1}) is present both in DMF and DMF-d_1, showing that this band is not due to aldehydic C–H bending vibration. These expected assignments are realised only in the results of MUBF. Notably, the 1395 cm^{-1} band has the assignment as C–H bending vibration in UBF and SVF, which is incorrect as discussed above.

Out-of-plane Vibrations: A brief mention is made here of the out-of-plane vibrations for completeness, although no calculations were made to aid the assignments. In the region under study, seven A'' vibrations are expected. Since the spectrum is of the liquid, some of the methyl group modes may overlap. Further, since some of the out-of-plane vibrations are weak, it may not be possible to observe them.

The band at 350 cm^{-1} is assigned to C′NC′ wagging mode (may also be associated with C–N torsional mode). The C=O wagging vibration is expected near 550—600 cm^{-1}; but no band is observed in this region. Similarly, the C–H wagging mode expected at 900—1100 cm^{-1} is not observed. The intensities of these bands are probably too weak to be observed or the bands might have merged with the neighbouring absorptions. The weak band at 1150 cm^{-1} is assigned to CH_3 wagging mode.[3)] Another out-of-plane rocking mode expected for A'' species may be too weak to be observed or may be taken to have merged with 1067 cm^{-1} band belonging to A' vibrations.[10)] The CH_3 deformation vibrations may be taken to have overlapped with 1460 and 1410 cm^{-1} bands of the A' vibrations. These features are commonly encountered in other similar molecules.[19,20,23)]

Dimethylformamide-^{15}*N*. The observed and calculated frequencies for DMF-^{15}N are given in Table 5 along with their assignments. It is interesting to observe the changes in the assignments as compared to those of DMF, particularly with respect to C–N stretching mode.

Dimethylformamide-d_7. The calculated frequencies obtained for DMF-d_7 using the same force constants as those of DMF are given in Table 5 along with the observed frequencies. Two points worth noting are: the absence of 1512 cm^{-1} frequency in the infrared spectrum of DMF-d_7 and the appearance of pure C–N stretching vibration at 1385 cm^{-1}. A detailed picture of the changes due to complete deuteration of DMF can be obtained from the same Table .

Force Fields. The UBF force constants of formamide and *N*-methylformamide,[2)] and MUBF force constants of *N*-methylacetamide[24)] formed the starting point for UBF and MUBF calculations of DMF.

There is considerable difference between the observed and the calculated frequencies due to methyl rocking modes in the UBF. The difficulties of reproducing the rocking frequencies in this force field are well known.[2,23)] Some unacceptable assignments in the UBF and SVF (where a number of interaction constants are neglected) may reflect upon the inadequacies of these force fields. The frequency-fit alone cannot be a criterion in judging the suitability of a force field and therefore, while making a choice among the force fields, the reproducibility of the data from the frequency shifts in isotopic molecules should be kept in view. Such data could be useful in making correct assignments.[25)] The results of the MUBF for DMF are in good agreement, as discussed before, with the frequency shifts from the isotopic species, DMF-^{15}N, DMF-d_1 and DMF-d_7; whereas the results from the other two force fields are not. Only the assignments from MUBF are, therefore, given (Table 5).

Dimethylthioformamide. The UBF force constants for DMTF are transferred from thioformamide,[2)] *N*-methylthioformamide[2)] and DMF. The appropriate SVF force constants are taken from DMF. The assignments for DMTF are very nearly the same both in UBF and SVF. Frequency shifts from isotopic substitution are not available for DMTF to test the validity of the force fields, and the MUBF was not attempted in this case.

The assignments from the calculations are discussed here briefly. The symmetric and asymmetric C′–N stretching at 828 and 1212 cm^{-1} compare well with

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24) The authors are not in possession of the spectrum of DMF-d_1.

25) J. Jakes and B. Schneider, *Coll. Czech. Chem. Commun.*, **33**, 643 (1968).

26) L. H. Jones, L. B. Asprey, and R. R. Ryan, *J. Chem. Phys.*, **47**, 3371 (1967).

those of DMF. In DMTF complexes of cobalt(II) and nickel(II) chlorides,[27] the bands at 1560 and 521 cm^{-1} in DMTF shift to higher frequencies to around 1580 and 535 cm^{-1}, respectively and the band at 975 cm^{-1} shifts to lower frequencies to 950 cm^{-1}. These shifts agree with the assignments made for the bands at 1560, 521, and 975 cm^{-1} to C–N stretching, coupled C=S bending and C=S stretcing vibrations, respectively. The band at 1130 cm^{-1} is due to a CH_3 rocking vibration coupled with C=S and C–N stretching vibrations. This mode, being sensitive, shifts to higher frequencies in metal complexes and on *S*-methylation.[28]

Jensen and Nielsen[28] have studied the infrared absorption bands of a series of thioamides and located the characteristic bands. Recently, Indirachary and Ramaiah[29] have made a normal coordinate analysis of DMTF, treating the methyl groups as point masses. In particular, the bands at 970, 915, and 518 cm^{-1} have been assigned to C–H out-of-plane bending, C=S stretching and C′NC′ bending vibrations, respectively.[29] These assignments differ from the present ones. The band at 922 cm^{-1} can be assigned to the out-of-plane bending mode of C–H.

Dimethylselenoformamide. In a series of thioamides and related selenoamides, Jensen and Nielsen[28] observed that the substitution of sulphur with selenium behaves like 'isotopic substitution' and shifts the C=S stretching by 30—100 cm^{-1} towards lower frequencies, while the other frequencies are generally unaltered. Employing the force constants of DMTF, approximate calculations have been made for DMSeF. The calculated frequencies show the expected trend. The C=Se stretching and bending are expected around 930 and 497 cm^{-1} respectively, according to the present calculations.

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[27] G. Durgaprasad and C. C. Patel, unpublished data.

[28] K. A. Jensen and P. H. Nielsen, *Acta Chem. Scand.*, **20**, 597 (1966).

[29] C. A. Indirachary and K. V. Ramaiah, *Proc. Indian Acad. Sci.*, **69A**, 18 (1969).