While coins of copper-tin alloy and copper-tin-silver alloy are known. fusion of iron either in bronze or in copper, or the use of iron core for the purpose of minting coins has not been so far recorded. Paunar coins are the first to reveal these alloys and the iron core in ancient coinage.

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VIBRATIONAL SPECTRA AND NORMAL VIBRATIONS OF N-METHYLTHIOACETAMIDE

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INTRODUCTION

SPECTROSCOPIC studies of primary, secondary and tertiary amides received considerable attention. Studies of intermolecular associations[1], dichronic absorption studies[2], band contour studies of the vapour spectra[3], measurement of integrated intensities of the absorption bands arising out of the stretching vibrations of the C=O and N-H groups[4,5] and normal co-ordinate analysis[6-10] gave information regarding the nature of the functional groups, orbital interactions and mixing of the skeletal frequencies arising out of the inplane modes of vibration.

In recent times, spectra of some primary, secondray and tertiary thioamides[11,6,10] have been recorded and normal co-ordinate treatment of some of these molecules has been carried out to assign the C-N and the C=S stretching frequencies and estimate the magnitude of the coupling between these modes of vibration and to compare these results with those obtained of C-N and C=O stretching modes in the corresponding amides[7].

EXPERIMENTAL AND NORMAL CO-ORDINATE TREATMENT

The authors have recorded the infrared spectra of N-methylthioacetamide and its N-deuterated species and have carried out the normal co-ordinate treatment in order to clarify the nature of the absorption bands arising out of the inplane modes of vibration and compare these results with those of N-methyl-acetamide obtained by the earlier workers. The frequencies of the functional groups of the N-methylthioacetamide and N-deuterated N-methylthioacetamide are given in Table I.

TABLE I

N-Methylthioacetamide		N-Deuterated N-methylthio-acetamide	
Mode of vibration	Frequency	Mode of vibration	Frequency
ν (N-H) ..	3283	ν (N-D) ..	2380
Amide II Band	1560	Amide II Band	1510
,, III ,,	1360	,, III ,,	1260
ν (C=S) ..	690	ν (C=S) ..	680
δ (N-H) $\perp$ ..	740	δ (N-D) $\perp$ ..	515

The corresponding frequencies of N-methyl-acetamide and N-deuterated N-methylacetamide obtained by the earlier workers[12] are given in Table II for comparison.

TABLE II

N-Methylacetamide		N-Deuterated N-methyl-acetamide	
Mode of vibration	Frequency	Mode of vibration	Frequency
ν (N-H) ..	3330	ν (N-D) ..	2475
Amide II Band	1558	Amide II Band	1479
,, III ,,	1300	,, III ,,	1120
ν (C=O) ..	1647	ν (C=O) ..	1639
δ (N-H) $\perp$ ..	705	δ (N-D) $\perp$ ..	520

The frequency of the amide III band in N-methylthioacetamide is at 1360 cm^{-1} while the corresponding absorption in N-methylacetamide occurs at 1300 cm^{-1}, but the same absorption occurs at 1260 cm^{-1} in N-deuterated N-methylthioacetamide and at 1120 cm^{-1} in N-deuterated N-methylacetamide. On the other hand, the amide II, absorption occurs almost at the same frequency both in N-methylthioacetamide and N-methylacetamide, but at different frequencies in their deuterated species. It is also important to mention that the ν (N-H)

and ν (N–D) frequencies in N-methylthioacet-amide have lower values compared to those of the corresponding frequencies in N-methyl-acetamide.

N-methylthioacetamide is treated as a six-body problem taking CH_3 group as a point mass. The structure of N-methylthioacetamide is shown is Fig. 1.
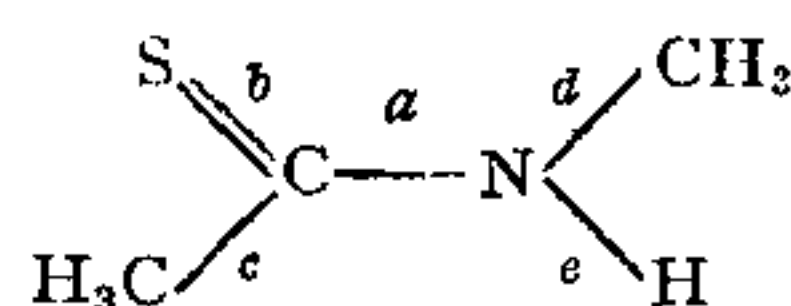

FIG. 1

The molecule belongs to the point group Cs and the twelve fundamentals which are classified as nine inplane (A') and three out of plane (A") vibrations are active both in the infrared and Raman spectra. The orthonormalised set of symmetry co-ordinates for the inplane vibra-tions of the molecule is given in Table III.

TABLE III

Symmetry co-ordinates		Vibrational mode
$R_1 = \triangle a$	..	ν (C–N)
$R_2 = \triangle b$	..	ν (C=S)
$R_3 = \triangle c$	..	ν (C–CH$_3$)
$R_4 = \triangle d$	..	ν (N–CH$_3$)
$R_5 = \triangle e$	..	ν (N–H)
$R_6 = 1/\sqrt{6}\ (2\triangle ab - \triangle ca - \triangle bc)$	..	δ (S=C–N)
$R_7 = 1/\sqrt{2}\ (\triangle bc - \triangle ac)$	..	γ (C–CH$_3$)
$R_8 = 1/\sqrt{6}\ (2\triangle ad - \triangle de - \triangle ae)$	..	δ (N–CH$_3$)
$R_9 = 1/\sqrt{2}\ (\triangle ae - \triangle ed)$	..	δ (N–H)

The expressions for the elements of the F and the G matrices are obtained in the usual way and the structure parameters used in these computations are : γ (C=S) = 1·713 Å, γ (C–N) = 1·29 Å, γ (N–H) = 1·07 Å, and γ (C–CH$_3$) = 1·55 Å. All the bond angles are assumed as 120°. General quadratic potential function is the force field used in these calculations.

The secular determinant which has the dimensionality of 9 × 9 has been solved by the modified Danielewsky's method using a pro-gramme written in Fortran language for Model 2, IBM 1620 digital computer. General pro-gramme of IBM 1620 was used to extract the roots of the polynominal.

The force constants proposed in related molecules were transferred and they were varied to obtain a close fit between the observed and calculated frequencies. The final set of force constants used in these calculations are given in Table IV. The observed, calculated frequencies and the potential energy distribu-tion of each normal mode among various symmetry co-ordinates as obtained in these computations are given in Table V. Similar results obtained by Miyazawa et al.[7] in case of N-methylacetamide are given in Table VI for comparison.

TABLE IV
Force constants

$f_a = 7$	$f_{ae} = 0\cdot3$
$f_b = 4$	$f_{ad} = 1\cdot8$
$f_c = 4\cdot3$	$f_a^b = 0\cdot32$
$f_d = 5$	$f_b^c = 1\cdot2$
$f_e = 6$	$f_a^c = 1\cdot2$
$f_{ab} = 0\cdot34$	$f_c^{bc} = 0\cdot9$
$f_{bc} = 0\cdot9$	$f_c^{ca} = 0\cdot6$
$f_{ca} = 0\cdot8$	

Bond stretching and bond–bond interaction constants are in md/A, bond-angle interaction constants are in md/γad and bond-bending con-stants are in md A/γad².

Although the N–H stretching frequency is high compared to the remaining skeletal

TABLE V
Potential energy distribution of different modes of vibration among various symmetry co-ordinates of N-methylthioacetamide

Mode of vibration	Frequencies (cm^{-1})		Potential energy distribution								
	Observed	Calculated	R_1	R_2	R_3	R_4	R_5	R_6	R_7	R_8	R_9
Amide III	1360	1315	21	14	2	0	0	1	10	6	43
ν (C=S)	690	709	16	61	7	4	0	2	4	2	2
ν (C–CH$_3$)	950	941	3	0	75	13	0	0	0	11	0
ν (N–CH$_3$)	1100	1120	4	0	1	60	0	3	1	22	21
ν (N–H)	3283	3300	0	0	0	0	99	0	0	0	0
δ (S=C–N)	..	176	5	0	2	0	0	85	0	14	0
γ (C–CH$_3$)	370	350	0	17	0	4	0	0	77	0	0
δ (N–CH$_3$)	555	582	2	7	11	10	0	7	5	53	1
Amide II	1547	1557	46	3	1	10	0	0	2	2	36

TABLE VI

Potential energy distribution of different modes of vibration among various symmetry co-ordinates of N-methylacetamide

Mode of vibration	Frequencies (cm^{-1})		Potential energy distribution							
	Observed	Calculated	R_1	R_2	R_3	R_4	R_5	R_6	R_7	R_8
Amide III	1299	1296	35	9	22	1	12	1	0	29
ν (C=O)	1653	1644	10	78	4	0	3	6	3	9
ν (C-CH$_3$)	881	954	11	11	37	0	18	0	11	0
ν (N-CH$_3$)	1016	1006	1	1	7	78	1	4	5	1
δ (O=C-N)	627	602	1	1	28	7	42	9	9	0
γ (C-CH$_3$)	436	436	5	2	1	8	0	74	6	1
δ (N-CH$_3$)	289	279	0	0	0	0	26	7	67	0
Amide II	1567	1509	44	3	3	6	4	1	0	63

frequencies, it has been taken by the authors into consideration for the normal co-ordinate treatment. On the other hand, it has been separated out from the other frequencies by Miyazawa *et al.* in case of N-methylacetamide.

DISCUSSION OF THE NATURE OF THE ABSORPTION BANDS

The amide II and the amide III absorption bands in N-methylthioacetamide which are in the region of 1547 cm^{-1} and 1360 cm^{-1} arise out of the combined contribution of δ (N-H) and ν (C-N) vibrations. This result is similar to that of N-methylacetamide as indicated by the potential energy distribution given in Tables V and VI. It is significant to note that in the case of N-methylthioacetamide to the absorption at 1547 cm^{-1}, the contribution of ν (C-N) is higher than that of N-H deformation. Similarly to the frequency at 1360 cm^{-1}, the contribution of δ (N-H) is considerably higher than that of ν (C-N) vibration. These results are different from those obtained by Miyazawa *et al.* in the case of N-methylacetamide. In this case, to the amide II bands the contribution of δ (N-H) is more than that of ν (C-N) and to the amide III band, the contribution of ν (C-N) is higher than that of δ (N-H). This may explain the smaller variation in the frequencies of the amide II and the amide III absorption bands on deuteration of N-methylthioacetamide.

The band at 690 cm^{-1} is due to ν (C=S) and the contribution of the amide III frequency to this absorption is considerable. Similar result has been obtained by Miyazawa *et al.* in case of ν (C=O) and the amide III absorption frequencies as seen from the potential energy distribution given in Table VI.

The bands at 950 cm^{-1} and 1100 cm^{-1} are assigned to C-CH$_3$ and N-CH$_3$ stretching vibra-

tions respectively and there is almost no coupling between these two modes of vibration. The absorption at 3300 cm^{-1} is due to the N-H stretching vibration and it is significant to note that there is no contribution of any other mode of vibration to this frequency.

The frequency at 176 cm^{-1} is due to the δ (S=C-N) vibration and this result is in agreement with that obtained by earlier workers in the case of tertiary thioamides[10]. The bands at 555 cm^{-1} and 370 cm^{-1} are assigned to δ (N-CH$_3$) and γ (C-CH$_3$) vibrations respectively. γ (C-CH$_3$) and ν (N-CH$_3$) are contributing to the δ (N-CH$_3$) vibration while to the γ (C-CH$_3$), the contribution of the C=S stretching vibration is considerable. On the other hand, in case of N-methylacetamide, δ (O=C-N) makes substantial contribution to δ (N-CH$_3$). Similarly ν (N-CH$_3$) contributes to γ (C-CH$_3$) vibration. This may explain the considerable difference in the values of the frequencies of δ (N-CH$_3$) and γ (C-CH$_3$) vibrations in N-methylthioacetamde and N-methylacetamide.

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