

Vibrational spectra and normal coordinate treatment of N,N-dimethylthioacetamide

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Abstract. The infrared spectra and the Raman spectrum of N,N-dimethylthioacetamide are recorded. Normal coordinate treatment of N,N-dimethylthioacetamide is carried out and the force constants are refined by the damped least squares technique. The potential energy distributions in both general quadratic space and symmetry coordinates are computed. Vibrational assignments of all the in-plane vibrations and some of the out-of-plane vibrations are made. The nature of the absorption bands is discussed in relation to the mixing of the skeletal modes of vibration. The vibrational mean amplitudes are also calculated.

Keywords. Vibrational spectra ; normal coordinate treatment ; N,N-Dimethylthioacetamide.

1. Introduction

The vibrational spectra of N,N-dimethylthioacetamide (DMTA) have been recorded and frequencies have been assigned on the basis of normal coordinate treatment by different workers. Indirachary and Venkata Ramiah (1969) and Desseyn and Le Poivre (1975) used general valence force field (GVFF), treating the CH_3 groups as mass points in the normal vibrational analysis of DMTA. This could at best be an approximation as the potential energy contribution of CH_3 deformational modes to other vibrational modes of the molecule has been neglected. Ray and Satyanarayana (1972) used Urey-Bradley force field (UBFF) for the normal coordinate analysis of complete molecular model of DMTA but eliminated C-H stretching vibrations from the calculations. They could not obtain a good frequency fit for rocking vibrations of the methyl groups which was attributed to the UBFF. No attempt was made to assign the out-of-plane vibrations of DMTA on the basis of normal coordinate analysis. We therefore considered it worthwhile to study the vibrational analysis of complete molecular model of DMTA including C-H stretching vibrations using GVFF to assign as many vibrational frequencies as possible.

2. Experimental

The IR spectrum of DMTA is recorded in the region between 4000–250 cm^{-1} with a Perkin-Elmer Model 521 grating spectrophotometer using mull and KBr pellet techniques. The spectra of the same thioamide are recorded in moderately concentrated and highly concentrated solutions of chloroform using matched cells of 0.05 mm thickness with CsBr windows. The low frequencies of the thioamide are taken from the Raman spectrum recorded by using the Hilger Raman source unit.

3. Normal coordinate treatment

The method of Wilson (1939, 1941) is used to calculate the GVFF. It is assumed that DMTA has a planar structure with point group C_s . It is also assumed that two of the hydrogens of each (CH_3) group lie out of the plane of molecular symmetry, one below and the other above the plane. In C_s structure the 39 fundamental vibrations fall into 24 in-plane vibrations of A' species and 15 out-of-plane vibrations of A'' species. In this paper the vibrations of A' species have been treated completely whereas the A'' species could be treated only partially. The structure of the molecule is shown in figure 1. The structure parameters are the same as those employed by Indirachary and Venkata Ramiah (1969). The angles around the methyl carbon atoms are assumed to be tetrahedral with C–H bond length equal to 1.08 Å. The symmetry coordinates of $-\text{N}(\text{CH}_3)_2$ group are the same as used for N,N-dimethyl acrylamide (Ramana Rao and Venkata Ramiah 1980) and those of the remaining part are taken from N-methylacetamide (Bhupal Reddy *et al* 1978).

The computing procedure is similar to that used for acrylamide (Ramana Rao *et al* 1975). To get the initial set of force constants, the constants of CH_3 groups

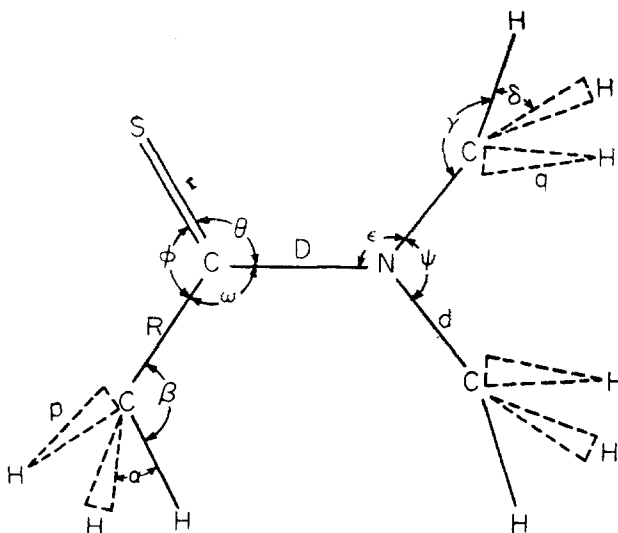


Figure 1. Structure of N,N-dimethylthioacetamide.

are taken from N-methylacetamide (Bhupal Reddy *et al* 1978) and the remaining transferred from DMTA skeletal calculations (Indirachary and Venkata Ramiah 1969). Thirty-three frequencies of DMTA are used to refine 23 force constants by the damped least squares method (Papousek *et al* 1965). To avoid difficulties of correlation of force constants due to redundant coordinates one of the bending force constants around the thiocarbonyl carbon atom is held fixed during refinement (Fuhrer *et al* 1976). After several iterations the calculated and observed deformational frequencies of methyl groups do not agree. Hence, the two interaction constants $F_{\beta,\beta}$ and $F_{\gamma,\gamma}$ are added to the original set. The refinement is continued till convergence. The final set of force constants is given in table 1.

4. Results

The observed and calculated frequencies, potential energy distributions (PED) and vibrational assignment for DMTA are shown in table 2.

The symmetrised vibrational mean amplitudes (Morino *et al* 1952, 1953; Morino and Hirohita 1955) for the linkages $\nu(\text{C-N})$, $\nu(\text{C=S})$, $\nu(\text{C-C})$, $\nu_s(\text{NC}_2)$, $\nu_{as}(\text{NC}_2)$, $\nu_{as}(\text{CH}_3)_2$, $\nu_s(\text{CH}_3)_2$, $\nu_{as}(\text{CH}_3)$ and $\nu_s(\text{CH}_3)$ of DMTA are 0.0453, 0.0426, 0.0585, 0.0438, 0.0547, 0.0797, 0.0782, 0.0799 and 0.0784 Å respectively. These values are in good agreement with those of related molecules (Ramana Rao *et al* 1978).

5. Discussion

5.1. Vibrational assignments and nature of absorption bands

Table 2 gives the nature of absorption bands in terms of mixing of vibrational modes. The number of fundamental stretching vibrations of the methyl groups in the dimethyl amino group usually exceeds the number of bands which can be attributed to this origin (Jensen *et al* 1971, 1972). However, according to the results of normal coordinate analysis on DMTA, the four asymmetric modes of $(\text{CH}_3)_2$ are within a narrow interval of 4 cm^{-1} (2930, 2928, 2926 and 2926 cm^{-1}). In the same way the two fundamentals due to symmetric modes of $(\text{CH}_3)_2$ are almost coincident near 2812 cm^{-1} . Similarly, the two asymmetric modes of the CH_3 group attached to the functional carbon are anticipated within a narrow interval of 2 cm^{-1} (2913 and 2911 cm^{-1}) whereas the symmetric mode is predicted near 2797 cm^{-1} .

The assignments given in table 2 follow this pattern. Thus the strong infrared band near 2935 cm^{-1} has been assigned to the four fundamentals (two each of A' and A'' species) due to asymmetric stretches of $(\text{CH}_3)_2$ whereas that at 2905 cm^{-1} has been attributed to the two fundamentals (one each of A' and A'' species) due to the asymmetric stretches of CH_3 group as indicated by normal coordinate analysis. Relatively weak I.R. band near 2805 cm^{-1} has been ascribed to the two symmetric stretches of $(\text{CH}_3)_2$ and also to the symmetric stretch of CH_3 . These assignments are reasonable when compared with their counterparts in some dimethyl compounds such as dimethylacetamide (Lagrange *et al* 1970; Lagrange and Forel 1971), dimethyl selenoformamide (Anthoni *et al* 1974), dimethyl

Table 1. Final force constants for N,N-dimethylthioacetamide.

Sl. No.	Symbol	Coordinates involved	Common atoms	Value ^(a)
Direct force constants				
<i>Stretch</i>				
1.	K_p	C-H		4.502
2.	K_d	C-H		4.549
3.	K_R	C-C		3.600
4.	K_D	C-N		6.184
5.	K_a	N-C		4.867
6.	K_r	C=S		5.915
<i>Bend</i>				
7.	H_α	\angle HCH		0.477
8.	H_β	\angle HCC		0.709
9.	H_γ	\angle NCH		0.758
10.	H_δ	\angle HCH		0.481
11.	H_ϕ	\angle SCN		0.342
12.	H_ω	\angle SCC		0.892
13.	H_θ	\angle CCN		0.698
14.	H_ϵ	\angle CNC		1.154
15.	H_ψ	\angle CNC		0.999
Interaction constants				
<i>Stretch-Stretch</i>				
16.	$F_{D,r}$	C-N, C=S	C	0.663
17.	$F_{D,R}$	C-N, C-C	C	1.084
18.	$F_{r,R}$	C=S, C-C	C	0.955
19.	$F_{\delta,d}$	N-C, N-C	N	0.881
<i>Stretch-Bend</i>				
20.	$F_{R,\omega}$	C-C, \angle CCN	C-C	0.642
21.	$F_{R,\phi}$	C-C, \angle CCS	C-C	0.894
22.	$F_{R,\beta}$	C-C, \angle CCH	C-C	0.135
23.	$F_{R,\gamma}$	N-C, \angle NCH	N-C	0.456
<i>Bend-Bend</i>				
24.	$F_{\gamma,\gamma}$	\angle NCH, \angle NCH	N-C	-0.045
25.	$F_{\beta,\beta}$	\angle CCH, \angle CCH	C-C	-0.064

^(a) Units of force constants are mdyne/Å, mdyne/rad and mdyne Å/rad².

Table 2. Potential energy distributions and vibrational assignments of N, N-dimethylthioacetamide^(a)

Observed frequency (cm ⁻¹)	Calculated frequency (cm ⁻¹)	PED in internal force constants	Vibrational assignments
1	2	3	4
<i>A' species</i>			
2935	2930	99K _q	99 ν _{as} (CH ₃) ₂
2935	2928	99K _q	99 ν _{as} (CH ₃) ₂
2905	2913	99K _p	99 ν _{as} (CH ₃) ₂
2805	2812	100K _q	100 ν _s (CH ₃) ₂
2805	2811	100K _q	100 ν _s (CH ₃) ₂
2805	2797	100K _p	100 ν _s (CH ₃) ₂
1510	1551	46K _D , 13H _γ , 10K _r , 10K _d	44ν(C-N) + 14γ(CH ₃) ₂ + 12ν _s (NC ₂)
1420	1404	53H _α , 30H _δ	53δ _{as} (CH ₃) + 25δ _{as} (CH ₃) ₂
1420	1431	53H _δ , 25H _γ	(34, 15) δ _{as} (CH ₃) ₂ + 15γ(CH ₃) ₂ + 11δ _s (CH ₃) ₂
1420	1422	56H _δ , 23H _α , 11H _γ	(29, 27) δ _{as} (CH ₃) ₂ + 23δ _{as} (CH ₃)
1385	1394	47H _δ , 27H _γ	44δ _s (CH ₃) ₂ + (18, 12) δ _{as} (CH ₃) ₂ ^(b)
1360	1359	56H _β , 38H _α , 10H _γ	82δ _s (CH ₃) ₂
1360	1353	67H _γ , 43H _δ	90δ _s (CH ₃) ₂
1275	1285	35H _γ , 25K _d , 22H _δ , 14K _r , 12H _e	28δ _s (CH ₃) ₂ + 12ν(C=S) + 11γ(NC ₂)
1175	1186	34H _γ , 31K _d , 13H _δ , 13H _β , 10K _r	18ν _{as} (NC ₂) + (16, 12) γ(CH ₃) ₂ + 14γ(CH ₃) + 10ν(C=S)
1050	1036	38H _γ , 27H _β , 19K _d	(29, 11) γ(CH ₃) ₂ + 29γ(CH ₃) + 11ν _{as} (NC ₂)
1050	1044	57H _γ , 14K _d , 10K _D , 10H _δ	(35, 25) γ(CH ₃) ₂
1010	987	34K _d , 34K _r , 22H _β , 14K _R	29ν(C=S) + 24γ(CH ₃) + 20ν _{as} (NC ₂)
862	862	64K _R , 33K _d , 22K _D	44ν(C-C) + 35ν _s (NC ₂) + 13ν(C-N)
660	691	32K _R , 22K _d , 11K _r	42ν(C-C) + 25ν _s (NC ₂) + 16ν(C=S) + 12ν(C-N)
490	464	36H _e , 28H _ψ , 13K _d	45δ(NC ₂) + 20γ(NC ₂) + 13δ(S=C-N)
438	427	35H _e , 18K _r , 16K _d , 14H _ψ , 10H _ω	27γ(NC ₂) + 22δ(NC ₂) + 18ν(C=S) + 15γ(C-C) + 12ν _{as} (NC ₂)
300	284	52H _φ , 19H _ω	64γ(C-C) + 17δ(NC ₂)
149	153	48H _φ , 39H _ω , 18H _e , 17H _φ , 17K _R	81δ(S=C-N) + 17γ(NC ₂)

Table 2.—(Contd.)

1	2	3	4
<i>A'' species</i>			
2935	2926	99K _q	99ν _{as} (CH ₃) ₂
2935	2926	99K _q	99ν _{as} (CH ₃) ₂
2905	2911	99K _p	100ν _{as} (CH ₃)
1420	1427	79H _δ , 20H _γ	79δ _{as} (CH ₃) ₂ + 21γ(CH ₃) ₂
1420	1418	84H _δ , 15H _γ	84δ _{as} (CH ₃) ₂ + 16γ(CH ₃) ₂
1420	1413	83H _α , 15H _β	83δ _{as} (CH ₃) + 17γ(CH ₃)
1175	1133	74H _γ , 21H _δ	78γ(CH ₃) ₂ + 21δ _{as} (CH ₃) ₂
1050	1086	76H _β , 17H _α	83γ(CH ₃) + 17δ _{as} (CH ₃)
1050	1084	79H _γ , 16H _δ	84γ(CH ₃) ₂ + 16δ _{as} (CH ₃) ₂

(a) Contributions below 10% are not shown. (b) (18, 12) δ_{as}(CH₃)₂ means that one of δ_{as}(CH₃)₂ contributes 18% whereas the other δ_{as}(CH₃)₂ contributes 12%. Similar meaning can be given to other expressions of the same kind.

diazinine (Mitchell and Merritt 1968), dimethyl sulphone (Uno *et al* 1971) and dimethyl acrylamide (Ramana Rao and Venkata Ramiah 1980). This is also confirmed by the PED given in table 2 as the corresponding symmetry coordinate contributes almost 100% of potential energy to these modes.

It could be seen from table 2 that only two out of the three rocking modes of A' type of CH₃ groups mix with the modes which are other than the internal modes of these groups. Some of the remaining methyl deformations mix with the internal modes of methyl groups only whereas the remaining mix neither with the internal modes of methyl groups nor with other vibrational modes.

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