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VIBRATIONAL SPECTRA, ASSIGNMENTS AND NORMAL COORDINATE ANALYSIS OF N,N-DIMETHYLTHIO-ACETAMIDE

S MOHAN† AND N SUNDARAGANESAN

Raman School of Physics, Pondicherry University, JIPMER Campus, Pondicherry-605006, India

AND

FERIDOUN PAYAMI

Department of Physics, Anna University, Madras-600025, India

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The Raman spectrum of N,N-Dimethylthioacetamide was recorded and its infrared spectrum as mulls was measured in the range 4000–200cm^{-1}. The frequencies were assigned to various fundamental modes on the basis of normal coordinate calculations. A 34-parameter modified valence force field has been employed for a normal coordinate analysis of N,N-Dimethylthioacetamide. A least-square technique was used to refine the force constants. The potential energy distribution was calculated. The nature of the absorption bands is discussed in relation to the mixing of vibrational frequencies.

Key Words: Vibrational Spectra; Assignments; Normal Coordinate Analysis; N-Dimethylthioacetamide

Introduction

The normal vibrations of primary, secondary and tertiary thioamides have been well investigated[1–3]. The vibrational spectra of the next higher thioacetamide, N,N-dimethylthioacetamide have been recorded and frequencies have been assigned by Ray and Sathyanarayana[4] on the basis of Urey-Bradley force field. But somehow they have eliminated C–H stretching vibrations from the calculations. They could not obtain a good frequency fit for rocking vibrations of methyl group which was attributed to use of UBFF. Indirachary and Venkata Ramiah[5], Desseyn and Le Poivre[6] and Bhupal Reddy[7] used general valence force field by assuming CH_3 groups as point mass in the normal coordinate analysis of DMTA. No attempt was made to assign all the vibrations of DMTA on the basis of normal coordinate analysis. The aim of the present investigation is to study the vibrational analysis of complete molecular model of DMTA including C – H stretching vibrations using GVFF to assign all the inplane and out of-plane vibrational frequencies.

†Author for correspondence.

Experimental

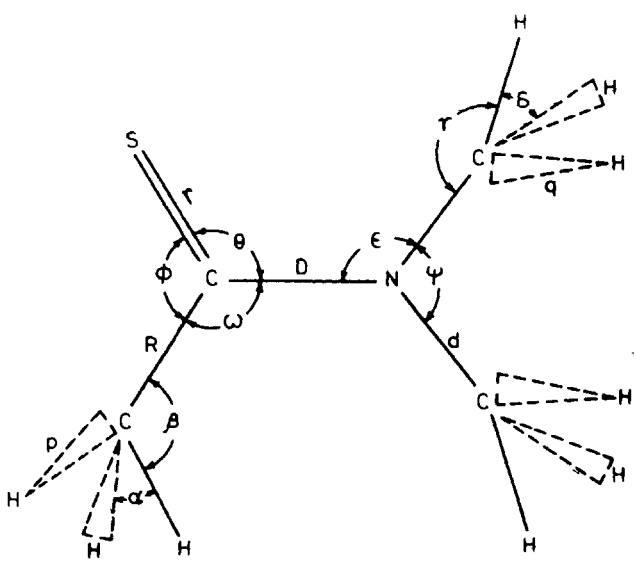
N,N-Dimethylthioacetamide was synthesized in the laboratory by treating high purity N,N-dimethyl acetamide with phosphorus pentasulphide in Benzene in accordance with the procedure suggested by Hofmann[8]. The infrared spectrum of the sample was recorded as mulls on a Perkin-Elmer 983 double beam grating spectrophotometer in the region 200–4000cm^{-1}.

The laser Raman spectrum of the liquid sample (in moderately concentrated solution of chloroform) was recorded in the standard 90° configuration in the region 100–4000cm^{-1}. A spectra-Physics Model 165 Ar^+ ion laser operating at 4W power continuously on the 488nm line was used as the laser source.

Scattered radiation was analysed using a Cary model 82 triple monochromator. Czerny-Littrow grating monochromators were used, two of these essentially give high dispersion and the third was arranged as an image of the second. The third reduced the stray light by several orders of magnitude. A spectral width of 20cm^{-1} was used. The spectra were measured with a scanning speed of 30cm^{-1} min^{-1}. The frequencies for all sharp bands are accurate to $\pm$ 1cm^{-1}.

Normal Coordinate Treatment

Wilson's FG matrix method was used for the normal coordinate analysis[9]. The molecule under investigation has C_s symmetry. A representative structure of the molecule is shown in Fig. 1. For a C_s structure, the 39 fundamental vibrations fall into 24 inplane vibrations of A′ species and 15 out of plane vibrations of A″ species. Further, it is 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 the present work, both inplane and out of plane vibrations are treated completely.



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The structural parameters employed in the present work are taken from Bhupal Reddy *et al*[7]. The initial set of force constants were taken from thioacetamide, N-methylthioacetamide (NMTA) and DMTF[1-3]. This set of force constants was subsequently refined by keeping few interaction constants fixed throughout the refinement process so that only 26 of the 34 force constants were refined.

Table I

Initial and final sets of force constants of N,N-dimethylthioacetamide (in units of mdyne Å^{-1} mydyne rad^{-1} and mdyne Å^{-1} rad^{-2}.)

Types of constants		Parameter	Coordinates involved	Initial	Final
Diagonal constants	Stretching	f_p	C – H	4.5000	4.5611
		f_q	C – H	4.5102	4.5726
		f_R	C – C	2.8500	3.4982
		f_D	C – N	6.421	6.0245
		f_d	N – C	5.7521	4.8791
		f_r	C = S	4.7411	5.9856
	Bending	f_α	HCH	0.251	0.2316
		f_β	HCH	0.554	0.5264
		f_γ	NCH	0.828	0.4922
		f_δ	HCH	0.256	0.2919
		f_ϕ	SCC	0.359	0.3410
		f_ω	CCN	0.508	0.6020
		f_θ	SCN	0.421	0.4114
		f_ε	CNC	0.751	0.7027
		f_ψ	CNC	0.759	0.7520
Interaction constants	Stretch	f_{Dr}	CN, CS	0.7131	0.7131
		f_{DR}	CN, CC	0.9126	1.1874
		f_{rR}	C = S, C – C	0.9519	0.9981
		f_{dd}	NC, NC	0.8105	0.7725
		f_{Dd}	CN, NC	0.6585	0.6585
	Stretch-bend	$f_{R\omega}$	CC CĈN	0.5141	0.5141
		$f_{R\phi}$	CC SCC	0.8216	0.9210
		$f_{R\beta}$	CC HĈC	0.8127	0.8127
		$f_{D\theta}$	CN SĈN	0.1021	0.1021
		$f_{D\varepsilon}$	CN CN̂C	0.0712	0.0895
		$f_{D\omega}$	CN CĈN	0.1211	0.0109
		$f_{d\psi}$	NC CNC	0.0091	0.0091
	bend-bend	$f_{\gamma\gamma}$	NĈH, NĈH	0.164	−0.0217
		$f_{\beta\beta}$	HĈC, HĈC	0.041	−0.0352
		$f_{\varepsilon\omega}$	CNC, CNC	0.1075	0.1075
		$f_{\theta\phi}$	SCN, SCR	0.0126	0.0021
		$f_{\phi\omega}$	SCR, CCN	0.0104	0.0104
		$f_{\omega\theta}$	CCN, NCS	0.0091	−0.0010

Table II *Potential energy distribution of N,N-dimethylthioacetamide*

Species	Observed frequency (cm^{-1})	Intensity	Calculated frequency (cm^{-1})	Vibrational assignment	PED%
a'	2938	S	2936	C – H asymm stretch in $(CH_3)_2$	$S_1(99)$
	2934	S	2934	C – H asymm stretch in $(CH_3)_2$	$S_2(100)$
	2910	M	2904	C – H asymm stretch in (CH_3)	$S_3(98)$
	2807	M	2806	C – H symm stretch in $(CH_3)_2$	$S_4(100)$
	2804	M	2802	C – H symm stretch in $(CH_3)_2$	$S_5(100)$
	2804	M	2801	C – H symm stretch in (CH_3)	$S_6(99)$
	1525	S	1529	C – N stretching	$S_7(71), S_{14}(11), S_{15}(10)$
	1430	M	1420	Asym $C(CH_3)$ deform	$S_8(54), S_{14}(21), S_{11}(10)$
	1422	M	1415	Asym $N(CH_3)_2$ deform	$S_9(49), S_{10}(49)$
	1420	W	1418	Asym $N(CH_3)_2$ deform	$S_{10}(59), S_8(23)$
	1390	M	1381	Sym $C(CH_3)$ deform	$S_{11}(81), S_8(11)$
	1373	W	1374	Sym $N(CH_3)_2$ deformation	$S_{12}(71), S_9(15)$
	1373	W	1370	Sym $N(CH_3)_2$ deformation	$S_{13}(68), S_{10}(22)$
	1280	W	1270	$C(CH_3)$ rocking	$S_9(22), S_{14}(42), S_{17}(12)$
	1176	M	1165	$N\langle^{(CH_3)}_{(CH_3)}$ asym stretching	$S_{15}(51), S_{20}(15), S_{16}(20)$
	1055	M	1050	$N(CH_3)$ rocking	$S_{16}(59), S_9(21), S_{13}(10)$
	1055	M	1042	$N(CH_3)$ rocking	$S_8(27), S_{17}(45), S_{12}(20)$
	1020	S	1025	C – S stretching	$S_{18}(82), S_{24}(10)$
	867	MS	860	C – C stretching	$S_{19}(79), S_{22}(10)$
	658	S	651	Sym $N\langle^{CH_3}_{CH_3}$ stretching	$S_{20}(71), S_{15}(15), S_{16}(10)$
	495	M	486	$N\langle^{CH_3}_{CH_3}$ deformation	$S_{16}(30), S_{13}(10), S_{21}(47)$
	440	M	431	CNC bending	$S_{22}(65), S_9(18)$
	300	M	308	$N\langle^{CH_3}_{CH_3}$ rocking	$S_{16}(18), S_{12}(24), S_{23}(42)$
	155	W	160	S = C – N deformation	$S_{24}(71), S_{18}(12)$
A"	2936	S	2931	$\nu_{asy}(CH_3)_2$	98 $\gamma_{asy}(CH_3)_2$
	2936	S	2931	$\nu_{asy}(CH_3)_2$	98 $\nu_{asy}(CH_3)_2$
	2905	S	2904	νasy(CH_3)	100 $\nu_{asy}(CH_3)$
	1415	M	1401	$\delta_{asy}(CH_3)_2$	75 $\delta_{asy}(CH_3)_2$, 25 $\gamma(CH_3)_2$
	1415	M	1401	$\delta_{asy}(CH_3)_2$	79 $\delta_{asy}(CH_3)_2$, 21 $\gamma(CH_3)_2$
	1415	M	1405	$\delta_{asy}(CH_3)$	81 $\delta_{asy}(CH_3)$, 19 $\gamma(CH_3)$
	1165	W	1161	$\gamma(CH_3)_2$	86 $\gamma(CH_3)_2$, 10 $\delta_{asy}(CH_3)_2$
	1150	M	1132	$\gamma(CH_3)$	71 $\gamma(CH_3)$, 19 $\delta_{asy}(CH_3)$
	1150	W	1135	$\gamma(CH_3)_2$	68 $\gamma(CH_3)_2$, 26 $\delta_{asy}(CH_3)_2$
	1060	M	1031	$\tau(CH_3)$ torsion	54 $\tau(CH_3)$, 22 $\omega(CH_3)$
	1045	W	1010	$\tau(CH_3)_2$	59 $\tau(CH_3)_2$, 10 $\omega(CH_3)$, 14 τ(C – N)
	1045	W	1010	$\tau(CH_3)_2$	59 $\tau(CH_3)_2$, 21 τ(C – N)
	1004	W	991	$\omega(CH_3)$	74 $\omega(CH_3)$, 10 $\tau(CH_3)$
	300	W	289	Wagging $C-N\langle^{CH_3}_{CH_3}$	78 $\gamma C-N\langle^{CH_3}_{CH_3}$
	202	VW	200	τ(C – N)	89 τ(C – N)

Contributions below 10% are not shown

S = Strong; M = Medium; MS = Medium Strong; W = Weak; VW = Very Weak

The final force constants are presented in Table I together with initial values. The potential energy distributions(PED) obtained using the final set of force constants are given in Table II, contributions below 10% are not shown. Table II also contains observed and calculated frequencies, nature of absorption bands in terms of mixing of vibrational modes, types of modes and vibrational assignments.

Results and Discussion

As expected the CH stretching vibrations around 2938 and 2907cm^{-1} are good group frequencies as the corresponding force constants contribute almost 100% to the PED of these modes. Hence the strong infrared band around 2938 has been assigned to Four asymmetric stretches of $(CH_3)_2$ $(2A' + 2A'')$ while the band at 2907cm^{-1} has been assigned to two asymmetric stretches of (CH_3) $(1A' + 1A'')$. The medium band around 2807cm^{-1} is assigned to two symmetric stretches of $(CH_3)_2$ and bond symmetric stretch of CH_3. In addition to PED confirmation these assignments compare very well with their counterparts in earlier work[10].

The strong band at 1525cm^{-1} is assigned to C – N stretching which agrees well with the literature values[3]. This frequency shows a mixing with the internal modes of methyl groups. As expected another strong band at 1020cm^{-1} is assigned to C = S stretching frequency. From Table II, it is clear that all the three rocking modes of A' type of CH groups mix with the modes, which are other than internal modes of this groups. C – C stretching is highly mixed with other vibrations and has contribution in the range 867cm^{-1}. The C – C stretching in the present work has been located at 867cm^{-1} in N,N-Dimethylthioacetamide. This value agrees well with N,N-Dimethyl acetamide[13].

The bands at 495 and 440cm^{-1} are predominantly to $N\langle^{CH_3}_{CH_3}$ deformation and C – $\hat{N}$ – C bending respectively. These values agree well with the literature values[1]. Further PED calculations support C – $\hat{N}$ – C bending vibration favourably. The asymmetric and symmetric deformations at 1430, 1390cm^{-1} respectively for C – (CH_3) group compare well with those in related molecules[1]. Similarly the asymmetric bending modes are easily located at 1422 and 1373cm^{-1}. It is not difficult to assign the other modes of vibration. Some of the vibrations of the A'' species have been assigned by comparing with the assignments in related systems and with the help of PED calculation. They are given in Table II along with vibrational assignments and PED.

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