VIBRATIONAL SPECTRA, ASSIGNMENTS AND NORMAL COORDINATE ANALYSIS OF N-METHYLACETAMIDE

S. Mohan* & N. Sundaraganesan

Raman School of Physics
Pondicherry University
JIPMER Campus
Pondicherry-605 006
INDIA

: الخلاصــة

تَمَّ تسجيل الطيف الرامانى لمادة (N-methylacetamide) ، وتَمَّ قياس طيف الأشعة تحت الحمراء في حيز (٢٠٠ - ٤٠٠٠ سم⁻¹)، وتَمَّ تحديد الترددات الأساسية المختلفة بواسطة قواعد الإحداثيات العادية. واستُخدِم مجال القوة التكافؤى ذي الثلاثين معاملاً لتحليل الإحداثيات العادية لمادة N-methylacetamide . واسُتخدِمت طريقة المربعات الصغرى لتحسين ثوابت القُوى. وتَمَّ أيضاً حساب توزيع جهد الطاقة. وقد نُوقشت طبيعة أحزمة الإمتصاص وعلاقتها بالترددات المهتزة الممتزجة.

ABSTRACT

The Raman spectrum of N-methylacetamide was recorded and its infrared spectrum as mulls was measured in the range 4000–200 cm^{-1}. The frequencies were assigned to various fundamental modes on the basis of normal coordinate calculations. A 30-parameter modified valence force field was employed for normal coordinate analysis of N-methylacetamide. A least-square technique was used to refine the force constants. The potential energy distribution was also calculated. The nature of the absorption bands is discussed in relation to the mixing of vibrational frequencies.

*To whom correspondence should be addressed.

VIBRATIONAL SPECTRA, ASSIGNMENTS AND NORMAL COORDINATE ANALYSIS OF *N*-METHYLACETAMIDE

INTRODUCTION

Miyazawa *et al.* [1] recorded the vibrational spectra of *N*-methylacetamide and carried out normal coordinate analysis using Urey–Bradley force field. Subsequently Jakes and Krimm [2] employed valence force field for the amide group to explain normal vibrations of nylon. Bradbury *et al.* [3] and Jakes *et al.* [4] have also attempted to explain the vibrational spectra of *N*-methylacetamide molecules. In all these works, the CH_3 group was considered as a point mass and the nature of the normal vibrations were not explained on the basis of potential energy distribution.

Hence the aim of the present investigation is to carry out the normal coordinate treatment of *N*-methylacetamide without treating the CH_3 group as a point mass and also employing the most general quadratic valence force field, using damped least squares method. As a consequence of this, the nature of the normal vibrations of *N*-methylacetamide appears to be more reliable.

EXPERIMENTAL

The infrared spectrum of the sample was recorded as mulls on Perkin–Elmer 983 double beam grating spectrophotometer in the region 200–4000 cm^{-1}. The laser Raman spectrum of the liquid sample (moderately concentrated solution in chloroform) was recorded in the standard 90° configuration in the region 100–4000 cm^{-1}. A Spectra-Physics model 165 Ar^+ ion laser operating at 4 W power continuously on the 488 nm line was used as the laser source.

Scattered radiation was analyzed 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
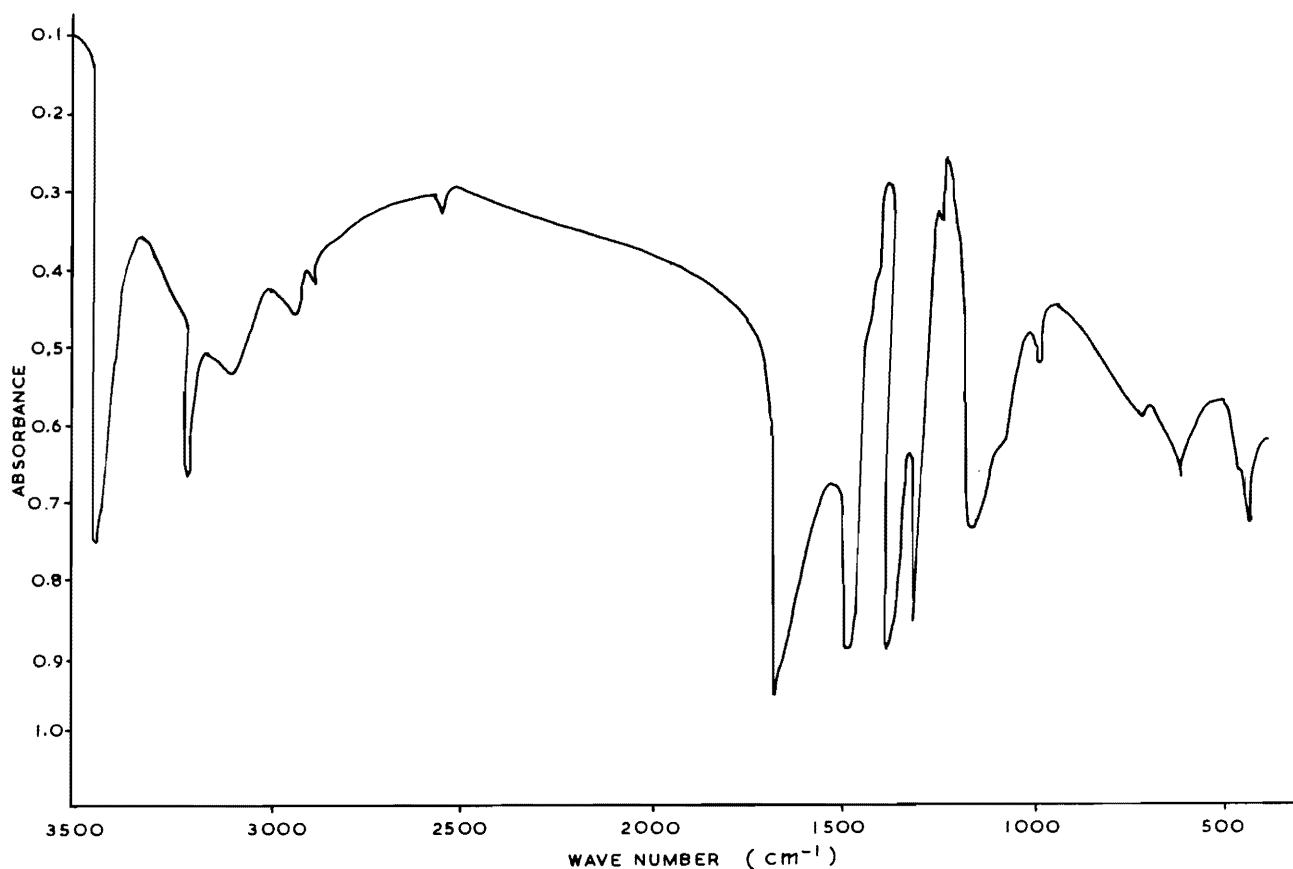

Figure 1. IR Spectrum of N-Methylacetamide.

the stray light by several orders of magnitude. A spectral width of 20 cm^{-1} was used. The spectra were measured with a scanning speed of 30 cm^{-1} min^{-1}. The frequencies for all sharp bands are accurate to ± 1 cm^{-1}. The observed IR and Raman spectra are shown in Figures 1 and 2 respectively.

NORMAL COORDINATE TREATMENT

Wilson's FG matrix method was used for the normal coordinate analysis [5]. The molecule under investigation has C_s symmetry. For a C_s structure, the 30 fundamental vibration fall into 19 in-plane vibrations of A' species and 11 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. A representative structure of the molecule is shown in Figure 3. In the present work, both in-plane and out-of-plane vibrations are treated completely.

The structural parameters employed in the present

work are taken from Bhupal Reddy *et al.* [6]. The initial set of force constants was taken from thioacetamide, *N*-methyl thioacetamide (NMTA) and DMTF [7–9]. This set of force constants was subsequently refined by keeping some interaction constants fixed throughout the refinement process so that only 24 of the 30 force constants were refined.

The final force constants are presented in Table 1 together with the initial values. The potential energy distributions (PED) obtained using the final set of force constants are given in Table 2, contributions below 10% are not shown. Table 2 contains observed and calculated frequencies, nature of the absorption bands in terms of mixing of vibrational modes, types of modes and vibrational assignments.

RESULTS AND DISCUSSION

As expected the free C–H stretching modes around 3104 and 2945 cm^{-1} are good group frequencies as the corresponding force constants contribute almost 100% to the PED of these modes. Hence the medium
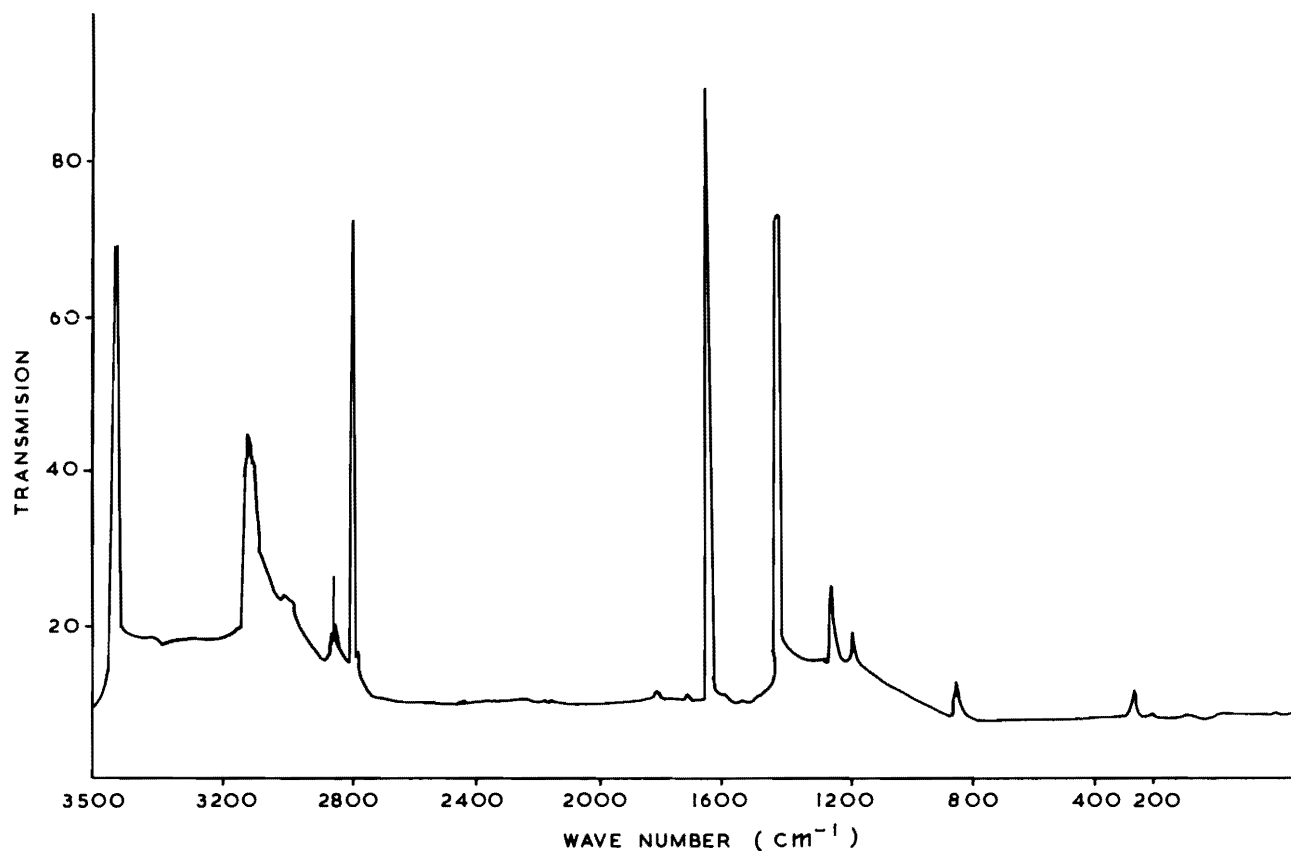

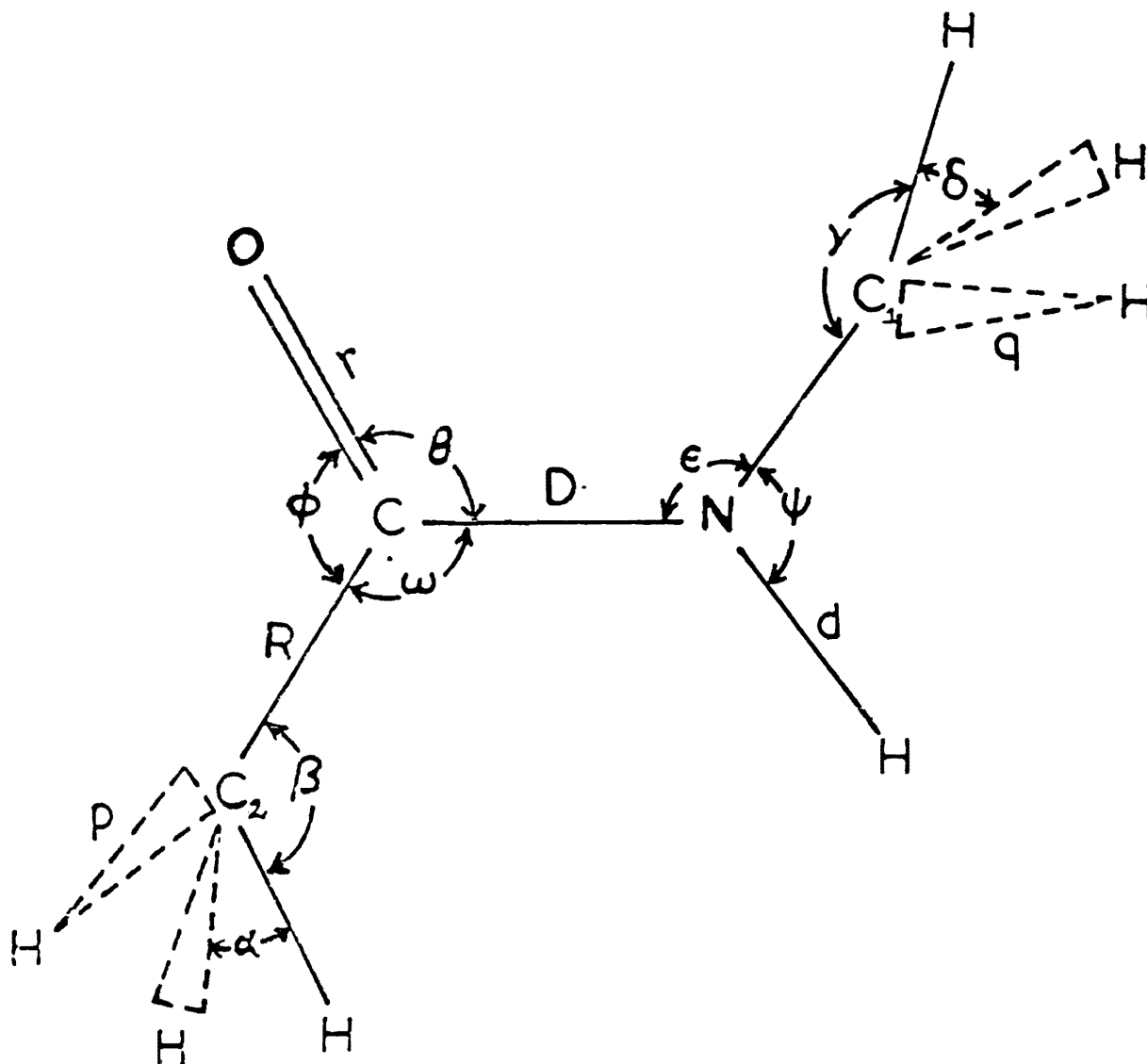*Figure 2. Laser Raman Spectrum of* N-Methylacetamide.

Figure 3. N-Methylacetamide.

infrared band around 3104 cm^{-1} has been assigned to two asymmetric stretches of $(CH_3)_2$ $(2A')$ while the band at 2945 cm^{-1} has been assigned to two symmetric stretches of $(CH_3)_2$. The very strong band at 3475 cm^{-1} is assigned to N-H stretching which is a free mode.

In the literature [1, 2] the band around 1093 cm^{-1} was assigned to $v(N-C_1)$ but Bradbury et al. [3] from their study did not support this assignment. Miyazawa [1] has not considered $v(NH)$ and $v(CH)$ modes of vibration and the deformation modes of CH_3 groups. The assignment made by Jakes et al. [2]

were only tentative. The present study supports the 996 cm^{-1} band to be assigned to N–C stretching vibration which agrees well with literature value [10]. Further there is no considerable contribution from (C_1H_3) as reported by Bhupal Reddy et al. [11]. An interesting result that emerges from the present study is the substantial contribution of C–N stretching and C–N–H deformation to the bands at 1490 cm^{-1} and 1251 cm^{-1} respectively. The earlier assignments [12] of 1500 cm^{-1} band to $v(C-N)$ in tertiary amides further supports the present C–N stretching assignment.

**Table 1. Initial and Final Sets of Force Constants of
N-methylacetamide.**

Typers of constants		Para-meter	Coordinates involved	Initial* value	Final value
Diagonal constants	Stretching[1]	f_p	C_2–H	4.5112	4.5701
		f_q	C_1–H	4.5102	4.5775
		f_R	C–C_2	3.4526	2.9500
		f_D	C–N	6.1126	6.4254
		f_d	N–H	6.0543	6.6521
		f_r	C=O	9.5874	9.5714
		f_e	N–C_1	4.0017	4.0610
	Bending[2]	f_α	HC_2H	0.2316	0.2316
		f_β	HC_2C	0.4260	0.6121
		f_γ	NC_1H	0.3500	0.2112
		f_δ	HC_1H	0.2919	0.2919
		f_ϕ	OCC_2	0.1610	0.2816
		f_ω	C_2CN	0.3150	0.4121
		f_θ	OCN	0.4520	0.3986
		f_ϵ	CNC_1	0.2620	0.4296
		f_ψ	C_1NH	0.3120	0.2229
Interaction constants	Stretch[3]–Stretch	f_{Dr}	CN, CO	0.6502	0.6596
		f_{DR}	CN, CC_2	1.1874	1.1874
		f_{de}	NH, NC	0.1210	0.2025
		f_{Dd}	CN, NH	0.4126	0.5928
	Stretch[4]–bend	$f_{R\beta}$	CC_2, HC_2C	0.1289	0.2854
		$f_{e\gamma}$	NC_1, NC_1H	0.1051	0.1947
		$f_{R\phi}$	CC_2, OCC_2	0.0981	0.1294
		$f_{R\omega}$	CC_2, C_2CN	0.5141	0.5141
		$f_{D\epsilon}$	CN, CNC_1	0.0895	0.0895
	Bend[5]–bend	$f_{\epsilon\psi}$	CNC_1, C_1NH	0.1075	0.1075
		$f_{\theta\omega}$	OCN, NCC_2	0.1126	0.1391
		$f_{\omega\phi}$	NCC_2, C_2CO	0.0926	0.0872
		$f_{\phi\theta}$	C_2CO, OCN	0.0356	0.0716

* Transfered from thioacetamide, N, N-Dimethylthioacetamide (NMTA) and DMTF.

[1,3] in mdyn Å^{-1}

[2,5] in mdyn Å rad^{-2} and

[4] in mdyn rad^{-1}.

Table 2. Potential Energy distribution of N-methylacetamide.

Species	Observed frequency (cm^{-1})	Intensity	Calculated frequency (cm^{-1})	Vibrational assignment	PED%
A'	3475	VS	3468	N–H stretching	$S_1(98)$
A'	3104 IR	M	3101	C–H asym stretch in (C_1H_3)	$S_2(100)$
A'	3104 IR	M	3100	C–H asym stretch in (C_2H_3)	$S_3(99)$
A'	2945 IR	M	2937	C–H symm stretch in (C_1H_3)	$S_4(98)$
A'	2945 IR	M	2937	C–H symm stretch in (C_1H_3)	$S_5(99)$
A'	1686	VS	1684	C=O stretching	$S_6(100)$
A'	1490	S	1481	C–N stretching	$S_7(78), S_{12}(10)$
A'	1438	VW	1433	Asym $C(CH_3)$ deformation	$S_8(58), S_{13}(21)$
A'	1438	VW	1435	Asym $N(CH_3)$ deformation	$S_9(61), S_{14}(22)$
A'	1405	S	1401	Sym $C(CH_3)$ deformation	$S_{10}(74), S_8(11)$
A'	1380	W	1371	Sym $N(CH_3)$ deformation	$S_{11}(64), S_9(20)$
A'	1251	W	1242	C–N–H deformation	$S_7(13), S_{12}(71), S_{17}(10)$
A'	1159	S	1151	$C(CH_3)$ rocking	$S_{13}(61), S_{10}(15), S_2(10)$
A'	1031	W	1024	$N(CH_3)$ rocking	$S_{14}(59), S_{11}(21), S_{12}(12)$
A'	996	W	991	$N-C_1$ stretching	$S_{15}(97)$
A'	874	VW	878	$C-C_2$ stretching	$S_{16}(98)$
A'	625	M	620	O=C–N deformation	$S_{17}(74), S_6(10)$
A'	431	MS	423	C_2CN bending	$S_{18}(71), S_9(20)$
A'	289	W	281	CNC_1CNC_1 bending	$S_{19}(68) S_9(14) S_{12}(10)$
A"	3186	MS	3179	$\nu_{asy}(CH_3)$	$97\nu_{as}(CH_3)$
A"	2983	VS	2975	$\nu_{asy}(CH_3)$	$98\nu_{as}(CH_3)$
A"	2932	VW	2921	$\delta_{asy}(CH_3)$	$70\delta_{as}(CH_3), 21\nu(CH_3)$
A"	2864	VW	2854	$\delta_{asy}(CH_3)$	$75\delta_{as}(CH_3) 18\nu(CH_3)$
A"	2521	W	2509	$\nu(CH_3)$	$85\nu(CH_3) 10\delta(CH_3)$
A"	2500	M	2504	$\nu(CH_3)$	$80\nu(CH_3) 15\delta(CH_3)$
A"	1364	S	1351	$\tau(CH_3)$	$54\tau(CH_3), 22\omega(CH_3)$
A"	1100	VW	1084	$\tau(CH_3)$	$61\tau(CH_3), 12\tau(C-N) 28\omega(CH_3)$
A'	724	W	718	$\omega(CH_3)$	$75\omega(CH_3), 10\tau(CH_3)$
A"	595	S	581	$\omega(CH_3)$	$64\omega(CH_3), 22\tau(CH_3)$
A"	205	VW	201	$\tau(C-N)$	$81\tau(C-N)$

Contributions below 10% are not shown.

VS – very strong, S – Strong, MS – Medium strong, M – Medium, W – Weak, VW – Very Weak

Although the bands at 625 cm^{-1}, 431 cm^{-1} and 289 cm^{-1} are of a mixed nature, they are mainly O=C–N deformation, $C_2\hat{C}N$ bending, and CNC_1 bending, respectively. As expected another strong band at 1686 cm^{-1} is assigned to C=O stretching mode and the corresponding force constants contribute 100% to the PED of this mode. From Table 1 it is clear that the rocking modes of A' type of CH groups mix with the modes which are other than internal modes of these groups. The C–C stretching in the present work has been located at 878 cm^{-1} in N-methylacetamide. This value agrees well with N,N-dimethylthioacetamide [13].

The band at 431 cm^{-1} is predominantly due to C_2CN bending. This value agrees well with literature value [7]. Further PED calculations support C_2CN bending vibrations favorably. The asymmetric and symmetric deformations at 1438 cm^{-1}, 1405 cm^{-1} respectively for C–(CH_3) groups compare well with those of related molecules. Similarly the asymmetric and symmetric deformations of N–(CH_3) groups are

easily located at 1435 cm^{-1} and 1371 cm^{-1} respectively. 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 calculations. They are given in Table 2 along with vibrational assignments and PED.

MEAN AMPLITUDE OF VIBRATION

The vibrational mean amplitudes evaluated at 298.16 K for the bonds C_2-H, C_1-H, C-C_2, C-N, N-N, C=O, and CN-C_1 of N-methylacetamide are ·7.73, 7.75, 5.86, 4.92, 7.10, 3.33, and 4.89 × 10^{-2} Å, respectively. These values agree well with those for related molecules [14].

CONCLUSION

A systematic analysis of infrared-Raman spectra of N-methylacetamide has been carried out through normal coordinate analysis. Further, the calculated potential energy distribution checks whether a chosen set of vibrational frequencies contributes maximum to the potential energy associated with the normal coordinates of molecule. Hence a complete analysis of N-methylacetamide is available in the present work.

ACKNOWLEDGEMENT

The authors are thankful to the learned referees for their constructive criticisms which improved the paper to the present form.

REFERENCES

[1] T. Miyazawa, T. Shimanouchi, and S. Mizushime, *J. Chem. Phys.*, **29** (1958), p. 611.

[2] J. Jakes and S. Krimm, *Spectrochim. Acta*, **27A** (1971), p. 19.

[3] E. M. Bradbury and A. Elliot, *Spectrochim. Acta*, **19** (1963), p. 995.

[4] J. Jakes and B. Schnider, *Coll. Czech. Chem. Commun.*, **33** (1968), p. 643.

[5] E. B. Wilson, Jr., *J. Chem. Phys.*, **7** (1939), p. 1047, **9** (1941), p. 76.

[6] T. Bhupal Reddy, G. Ramana Rao, and V. Venkata Chalapathi, *Proc. Indian Acad.*, **90** (1981), p. 35.

[7] I. Suzuki, *Bull. Chem. Soc. Japan*, **35** (1962), p. 1286, 1449, 1456.

[8] C. N. R. Rao and G. C. Chaturvedi, *Spectrochim. Acta*, **27A** (1971), p. 520.

[9] G. Durgaprasad and D. N. Satyanarayana, *Bull. Chem. Soc. Japan*, **44** (1971), p. 316.

[10] Arabinda Ray and D. N. Satyanarayana, *Bull. Chem. Soc. Japan*, **45** (1972), p. 2712.

[11] T. Bhupal Reddy, V. V. Chalapathi, and K. V. Ramaiah, *Indian J. Pure & Appl. Phys.*, **16** (1978), p. 652.

[12] V. V. Chalapathi and K. V. Ramaiah, *Proc. Indian. Acad. Sci.*, **68** (1968), p. 109.

[13] S. Mohan, N. Sundaraganesan, and Feridoun Payami, *Proc. Indian National Sci. Acad.* **56A** (1990), p. 567.

[14] G. Ramana Rao, V. Balasubramaniyan, and K. V. Ramaiah, *Indian J. Pure & Appl. Phys.*, **16** (1978), p. 657.