

# Ab initio studies on geometry and vibrational spectra of *N*-methylformamide and *N*-methylacetamide

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## Abstract

The molecular conformation, ground state molecular vibrations and force field of *N*-methylformamide (NMF) and *N*-methylacetamide (NMA) have been studied by the ab initio method at the Hartree–Fock level using the 6-31 + g\* basis set. The potential energy surface of NMA is investigated by the ab initio method with full geometry optimization. For both the molecules, *trans* conformer was found to be the most stable. For *trans*-NMF, methyl group in the staggered conformation and for *trans*-NMA, methyl groups in *cis*–*trans* position with respect to –CONH– group represent global minima. The vibrational spectral analysis has been carried out for both NMF and NMA. Comparisons with the previous assignments for amide bands have been made. The present results are compared with the previous results of structure and vibrational spectra and discussed. © 2002 Elsevier Science B.V. All rights reserved.

**Keywords:** *N*-Methylformamide; *N*-Methylacetamide; Ab initio method; Normal co-ordinate analysis

## 1. Introduction

*N*-Methylformamide (NMF) and *N*-methylacetamide (NMA) are the simplest molecular models containing the amide moiety characteristic of proteins and polypeptides [1,2]. Consequently an accurate description of the equilibrium geometry of NMF and NMA is helpful for understanding the geometric constraints imposed by the peptide linkages that determine, in part, the protein structure. NMF is also of considerable interest in medicine, since it possesses antitumor activity [3]. This paper describes briefly the results of an investigation of the molecular geometry, intramolecular harmonic force field and the vibra-

tional spectra of NMF and NMA in the ground state by the ab initio method at the Hartree–Fock level using a higher basis set, 6-31 + g\*.

Both NMF and NMA have been extensively studied both experimentally and theoretically. Ab initio calculations have been carried out to establish the geometry of isolated *trans*- and *cis*-forms of NMF and NMA [4–16]. With lower basis sets such as 4-21g and 4-31g, the fully optimized geometry obtained for NMF and NMA by the ab initio method was found to be planar [4–14]. However, with larger basis sets such as 4-31g\* and 6-31g\*, it was found that the equilibrium planar structure yielded one or two negative frequencies corresponding to the methyl torsion indicating that the planar structure was in fact a saddle point [4–16]. The MP2 level of calculation for NMA also yielded one negative eigen value corresponding to methyl torsion [15,16]. It clearly showed that the equilibrium structures derived by the ab initio method did not represent the global minima. The

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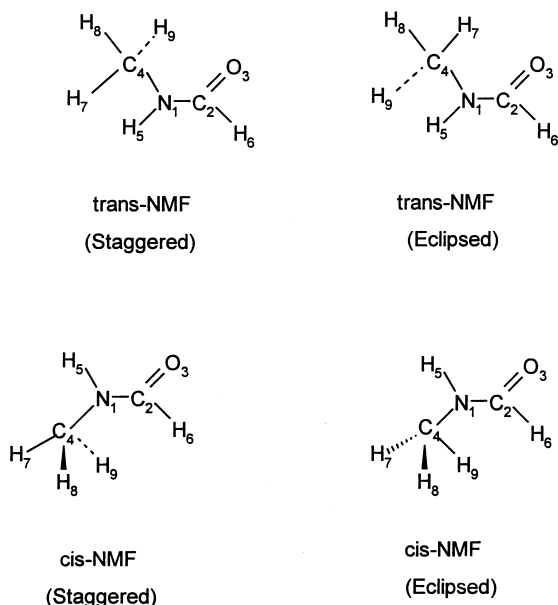


Fig. 1. Conformers of *N*-methylformamide.

presence of imaginary vibrational frequencies indicates that the symmetry imposed methyl group orientations leading to  $C_s$  symmetry for NMF and NMA represented unstable orientations. While the imaginary vibrational frequencies may have no effect on the in plane  $a'$  frequencies and the eigen vectors and a negligible effect on the higher frequencies of the out-of-plane  $a''$  modes, it does however influence the lower frequencies in the out of plane modes. In this context, it was of interest to carry out ab initio calculations of NMF and NMA at the Hartree–Fock (HF) level using a higher basis set 6-31 +  $g^*$  to determine the minimum energy equilibrium structure that would yield all the eigen values real. The vibrational spectra, band description and band intensities are then calculated and discussed in relation to the previous studies. The FT Raman spectra of NMF and NMA have been recorded and the data have been utilized in the discussion of the results.

## 2. Materials and methods

### 2.1. Ab initio calculations

The ab initio calculations at the HF level using the basis set 6-31 +  $g^*$  have been performed for NMF and

NMA employing GAUSSIAN 94 program [17]. First the fully optimized geometries of NMF and NMA were obtained by analytical gradient methods. The HF cartesian force constants, vibrational frequencies and their intensities were obtained analytically for the optimized geometry. The GMAT program of Schachtschneider [18] was employed to obtain the **B** and **G** matrices in internal coordinates for the optimized geometry. The atoms in Fig. 1 are numbered to define the optimized bond lengths and bond angles, and to specify the internal coordinates used in the calculation of vibrational spectra. The force constants in cartesian coordinates were transformed to force constants in local coordinates. Scaling of the force constants was made according to SQM method [19] in order to overcome the systematic overestimation of the force constants by the HF procedure. The force fields of NMF and NMA were also obtained in symmetry coordinates through appropriate transformations. The secular equation  $|\mathbf{GF} - E\lambda| = 0$  was then solved to obtain the vibrational frequencies and their potential energy distributions for NMF and NMA and also their deuterated molecules.

### 2.2. Spectroscopic measurements

The infrared spectra of NMF and NMA (Aldrich chemicals) were recorded on a FT infrared Bruker 5 spectrophotometer. The FT Raman spectra were recorded for the liquid sample taken in a silica capillary using Bruker RFS 100/s spectrometer employing  $\text{Nd}^{3+}$  YAG laser with 30 mW power at the sample, keeping the detector at liquid nitrogen temperature.

## 3. Results and discussion

### 3.1. Conformation

The structures of NMF and NMA have been extensively studied experimentally by means of X-ray [13,20–22], electron [20–23] and neutron diffraction [24,25] and inelastic neutron scattering methods [26] and theoretically by the molecular mechanics [27] and ab initio methods at the HF level using various basis sets [4–16] focusing the attention on *cis* and *trans* isomers arising from the restricted rotation about the C–N bond. In the liquid state, at ambient temperature the *trans* rotamer is predominately present both for

Table 1

Calculated total energies for the conformers of *trans*- and *cis*-NMF and NMA

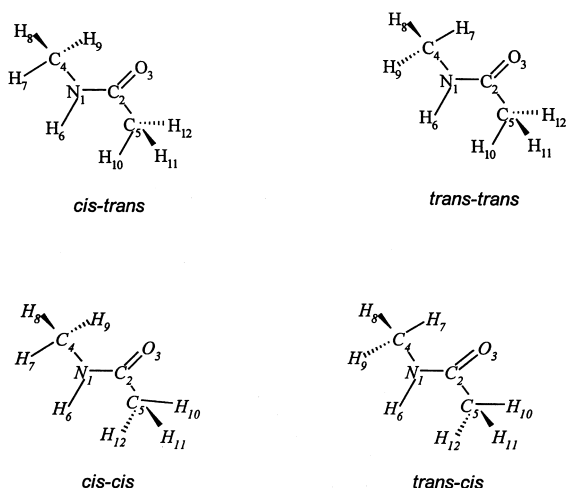
NMF conformer	Total energy (Hartree)	<i>trans</i> -NMA conformer	Total energy (Hartree)	<i>cis</i> -NMA conformer	Total energy (Hartree)
<i>trans</i>		<i>cis-trans</i>	– 247.0138514	<i>cis-trans</i>	– 247.0084297
Staggered	– 207.9688994	<i>trans-cis</i>	– 247.0129764	<i>trans-cis</i>	– 247.0087442
Eclipsed	– 207.968486	<i>trans-trans</i>	– 247.0132345	<i>Trans-trans</i>	– 246.760038
<i>cis</i>		<i>cis-cis</i>	– 247.0135737	<i>cis-cis</i>	– 247.0096788
Staggered	– 207.9658873				
Eclipsed	–207.966793				

Table 2

Optimized geometric parameters of *trans*- and *cis*-NMF and NMA

Parameters <sup>a</sup>	NMF			NMA		
	Expt [20]	Calculated		Expt [23]	Calculated	
		<i>trans</i>	<i>cis</i>		<i>trans</i>	<i>cis</i>
C–N	1.37	1.344	1.345	1.36	1.349	1.355
C=O	1.22	1.198	1.198	1.21	1.204	1.204
N–C	1.46	1.449	1.444	1.44	1.448	1.45
C–C				1.53	1.513	1.51
N–H	1.03	0.994	0.998		0.993	0.996
N(C–H <sup>b</sup> )	1.11	1.081	1.083	1.09	1.082	1.082
N(C–H <sup>c</sup> )	–	1.082	1.084	1.09	1.082	1.082
C–H	1.13	1.09	1.09			
C(C–H <sup>b</sup> )				1.09	1.084	1.079
C(C–H <sup>c</sup> )				1.09	1.083	1.085
N–C=O	124.6	124.75	124.96	125.0	122.11	121.3
H–C=O	112.7	122.00				
N–C–H		113.23	11.25			
N–C–C				113.0	116.5	116.6
O=C–C				–	121.4	121.89
C–N–C	121.4	122.12	125.27	107.0		127.28
C–N–H	118.7	118.39	118.99	–	119.35	118.5
H–N–C	119.9	119.49			118.97	114.19
N–C–H <sup>b</sup>		108.54	109.26	–	108.48	108.12
N–C–H <sup>c</sup>		110.78	111.15	–	110.86	112.06
H <sup>b</sup> –C–H <sup>c</sup>		109.11	108.15	–	110.86	107.89
H <sup>c</sup> –C–H <sup>c</sup>		108.49	108.86	–	108.38	107.89
C–C–H <sup>b</sup>					113.57	108.4
C–C–H <sup>c</sup>					108.57	110.98
H <sup>c</sup> –C–H <sup>c</sup>				–	107.75	109.3
H <sup>b</sup> –C–H <sup>c</sup>				–	109.1	107.8
C–N–C=O		0.0	180.0		0.0	180.0
C–C–N–H					0.0	180.0
H <sup>b</sup> –C–N–C		180.0	0.0		180.0	180.0
H <sup>c</sup> –C–N–C		– 60.23	– 60.72		60.2	– 61.22
H <sup>b</sup> –C–C–N					0.0	180.0
H <sup>c</sup> –C–C–N					121.55	–59.92

<sup>a</sup> Bond length in Angstroms and bond angle in degrees.<sup>b</sup> In-plane H atoms.<sup>c</sup> Out-of-plane H atoms.

Fig. 2. Conformers of *trans*-*N*-methylacetamide.

NMF and NMA. The total energies for the optimized geometries of NMF and NMA found with 6-31 +  $g^*$  split valence basis set are given in Table 1. The energy difference between the *trans* and *cis* conformers of NMF is about  $\sim 2.0$  kcal/mole in favor of the *trans* conformer which is in satisfactory agreement with the experimental value of  $\sim 1.6 \pm 0.3$  kcal/mole [4].

The present ab initio calculations have shown that the optimized equilibrium geometry of NMF has  $C_s$  symmetry. For *trans* NMF, the methyl group in the

staggered position has the minimum energy while for *cis*-NMF, the methyl group in eclipsed position as shown in Fig. 1 has the lowest energy. On the whole, *trans*-NMF with staggered methyl group orientation represents the global minima. The equilibrium geometrical parameters of the minimum energy conformation of the *trans* and *cis* isomers of NMF calculated with the basis set 6-31 +  $g^*$  are given in Table 2. Also given therein are the experimental parameters of NMF obtained from electron diffraction studies [20]. There is a good agreement between the calculated and experimental geometrical parameters. However the calculated bond angle of OCH deviates significantly from the observed value. For the *trans*- and *cis*-conformers of NMF, the calculated lowest vibrational frequency corresponding to NCH<sub>3</sub> torsion was positive for the staggered and eclipsed conformation of the methyl group, respectively, supporting that they represent the minimum energy conformations. Further, the eclipsed orientation of the methyl group in the *trans*- structure and the staggered orientation of the methyl group in the *cis* structure of NMF each yielded a negative eigen value corresponding to NCH<sub>3</sub> torsional mode showing that they represent the saddle points.

The conformation of *trans*- and *cis*-NMA shown in Figs. 2 and 3 can be characterized by the *cis* or *trans* relationship of an adjoining methyl group hydrogen atom to the C=O or N–H bond. The four conformers could be designated as *cis*–*trans*, *trans*–*trans*, *cis*–*cis* and *trans*–*cis* where the first term refers to the orientation of the H–N–C–H group. The total energies of the four conformers for which the equilibrium geometries were found with 6-31 +  $g^*$  split valence basis set are listed in Table 1 for the *trans* and *cis* conformers of NMA. The energy differences amongst these four different conformers of *trans*-NMA are very small, lie within  $\sim 0.8$  kJ/mole and the lowest energy conformation is *cis*–*trans*. The other optimized structures have CCH<sub>3</sub> dihedral angles that differ. The present ab initio calculations have yielded all positive eigen values for the *cis*–*trans* structure of *trans*-NMA and the optimized geometry possess  $C_s$  symmetry. The equilibrium geometrical parameters of the stablest *cis*–*trans* conformer of *trans*-NMA calculated with the basis set 6-31 +  $g^*$  are given in Table 2. Also given therein are the experimental parameters of NMA obtained from electron diffraction studies

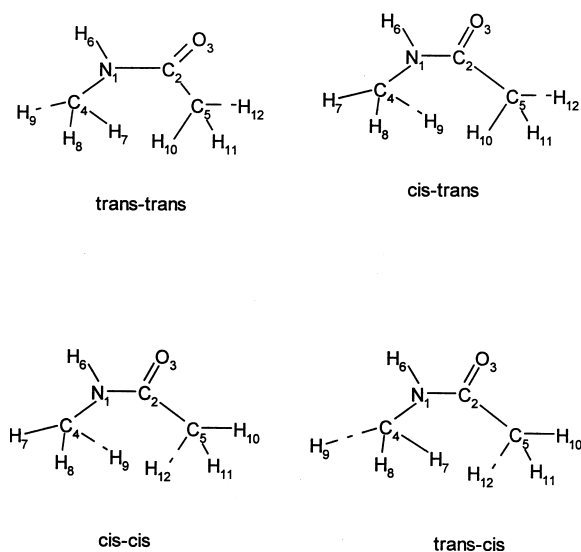
Fig. 3. Conformers of *cis*-*N*-methylacetamide.

Table 3

Experimental and calculated IR and Raman vibrational frequencies and band intensities (s = strong, v = very, m = medium, sh = shoulder, w = weak) for *trans*-NMF

IR		Raman		Assignment (PED) <sup>a</sup>	
Expt [29] $\nu$ (cm <sup>-1</sup> )	Calc. int <sup>b</sup>	Expt $\nu$ (cm <sup>-1</sup> )	Calc. int <sup>c</sup>	Calc. <sup>d</sup> $\nu$ (cm <sup>-1</sup> )	
<b>A' modes</b>					
3490m	49.7	3295w	66.9	3895	NHs(100)
2960w	28.5	2944vs	67.5	3313	NCH <sub>3</sub> as(99)
	25.4	2889s	139.7	3232	NCH <sub>3</sub> s(97)
2854mb	118.1	2860sh	103.4	3219	CHs(97)
1721vs	488.4	1655mw	11.8	1945	COs(74), CHb(13)
1528ms	222.7	1546w	222.7	1693	NHb(51), CNs(22)
1458w	13.3	1454w	5.25	1650	NCH <sub>3</sub> ad(75), NHb(10)
1410w	12.6	1414m	5.76	1605	NCH <sub>3</sub> sd(89)
1392w	11.5	1385m	5.7	1553	CHb(56), COb(33)
1207ms.	99.8	1246mw	3.6	1346	CNs(29), NCs(27), NHb(15)
1148w	7.6	1151w	1.7	1284	CH <sub>3</sub> r(54), NHb(15)
951mw	19.1	962ms	8.6	1030	NCs(66), CNs(23)
761vw	9.8	770vw	2.0	833	COb(42), CNCb(21), CH <sub>3</sub> r(15)
237w	13.6	297w	13.6	291	CNCb(69), COb(16)
<b>A'' modes</b>					
2944w	27.9	2944m	56.9	3298	CH <sub>3</sub> as(100)
1467vw	6.5	1454w	12.9	1625	CH <sub>3</sub> ad(91)
1148vvw	0.4	1151w	1.7	1262	CH <sub>3</sub> r(92)
880vw	3.3			1166	$\Pi_{CH}$ (95)
570m	27.5	621vw	1.3	505	$\tau_{CN}$ (82), $\omega_{NH}$ (11)
368mb	120.1	360mw	0.8	260	$\omega_{NH}$ (96)
		94s	0.2	61	$\tau_{CH_3}$ (53), $\omega_{NH}$ (21)

<sup>a</sup> s = symmetric stretch, as = asymmetric stretch, b = bend, sd = symmetric bend, ad = asymmetric bend, ob = out-of-plane bend, r = rocking,  $\tau$  = torsion.

<sup>b</sup> IR intensities in km/mole.

<sup>c</sup> Raman scattering activity in (a<sup>4</sup>)/amu.

<sup>d</sup> Unscaled frequencies.

[23]. There is good agreement between the calculated and experimental geometrical parameters. However the calculated HNC bond angle deviates significantly from the observed value as in the case of NMF. This deviation has also been noted in the previous ab initio studies [4].

For *cis*-NMA, the energy difference between the four conformers (Table 1) is large, about 15 kcal/mole, while the *cis*-*cis* conformer yielded one negative eigen value, the other three conformers yielded two or three negative eigen values. This demonstrates that *cis*-NMA is not a stable structure. The higher energy difference between the *cis*- and *trans*-NMA relative to *cis*- and *trans*-NMF may be attributed to the steric hindrance between the two methyl groups in the case of *cis*-NMA.

### 3.2. Vibrational spectra

The vibrational spectra of NMF have been of continued interest since the first paper by Suzuki [28] in 1962 who has carried out normal co-ordinate calculations for the in-plane vibrations of NMF. In recent years ab initio molecular orbital calculations have been performed using different basis sets such as 4-31g, 4-31g\* etc. at the HF level for both *trans*- and *cis*-conformers of NMF. However, in the previous work, as noted earlier one negative vibrational frequency was obtained for the higher basis set 6-31g\*. In the present work, the scaling of force constants was made by scaled quantum mechanical method [19]. Here, a scaled factor is obtained for each of the force constants as a quantitative measure

Table 4

Experimental and calculated IR and Raman vibrational frequencies and band intensities (s = strong, v = very, m = medium, sh = shoulder, w = weak) for *trans*-NMA

IR		Raman		Assignment (PED) <sup>a</sup>	
Expt [29] $\nu$ (cm <sup>-1</sup> )	Calc int <sup>b</sup>	Expt $\nu$ (cm <sup>-1</sup> )	Calc. int <sup>c</sup>	Calc. <sup>d</sup> (cm <sup>-1</sup> )	
<b>A' modes</b>					
3498m	43.2	3000sh	50.8	3866	NHs(100)
3008m	31.7	(3307) <sup>e</sup>	70.3	3335	CCH <sub>3</sub> as(93)
2973m	26.9	(3294) <sup>e</sup>	58.2	3307	NCH <sub>3</sub> as(94)
2958w	48.0	2935s	127.6	3219	CCH <sub>3</sub> s(78), NCH <sub>3</sub> (15)
2915w	13.2	(3223) <sup>e</sup>	121.8	3211	NCH <sub>3</sub> s(79), CCH <sub>3</sub> s(14)
1707vs	390.0	1651m	7.9	1934	COs(72)
1511s	322.5	(1667) <sup>e</sup>	4.8	1667	NCH <sub>3</sub> ad(69), NCH <sub>3</sub> r(13)
1446w	6.2	1449m	6.4	1630	NCH <sub>3</sub> sd(72), NCH <sub>3</sub> r(13)
1432m	20.3	(1626) <sup>e</sup>	6.4	1626	CCH <sub>3</sub> ad(71), CCH <sub>3</sub> sd(10)
1419w	6.5	1415m	5.9	1605	NCH <sub>3</sub> sd(85)
1370ms	25.7	1374w	3.4	1552	CCH <sub>3</sub> sd(78), CCH <sub>3</sub> ad(12)
1265s	120.9	1304m	5.6	1406	CNs(28), NHib(23), COb(13)
1168w	0.9	1161vw	1.0	1308	NCH <sub>3</sub> r(60)
1089w	6.9	1097vw	0.2	1189	NCs(54), CCH <sub>3</sub> r(19)
980w	16.1	990w	2.3	1094	CCH <sub>3</sub> r(49), CCs(24), NCs(13)
857mw	6.1	883m	8.1	948	CNs(26), NCH <sub>3</sub> r(17), CCs(16)
658w	10.5	629m	7.2	672	COb(40), CCs(33)
429m	10.5	440vw	0.75	458	NCCb(46), COb(29)
279w	7.5	287vw	0.25	284	CNCb(61), NCCb(29)
<b>A'' modes</b>					
3008m	8.5	(3301) <sup>e</sup>	64.2	3301	CCH <sub>3</sub> as(100)
2973w	29.6	2934s	58.4	3297	NCH <sub>3</sub> as(100)
1472w	6.6	(1625) <sup>e</sup>	12.7	1625	NCH <sub>3</sub> ad(91)
1432w	4.3	1449mw	9.5	1614	CCH <sub>3</sub> ad(92)
1185vw	0.7	(1262) <sup>e</sup>	1.8	1262	NCH <sub>3</sub> r(92)
1037w	9.7	1041vw	0.2	1169	CCH <sub>3</sub> r(72), $\Pi_{CO}$ (20)
619vw	2.3	629m	1.6	688	$\Pi_{CO}$ (68), CCH <sub>3</sub> r(24)
439s	103.7	439w	0.05	399	$\tau_{CN}$ (55), $\omega_{NH}$ (28)
(200) <sup>f</sup>	15.2	200sh	0.2	177	$\omega_{NH}$ (81), $\tau_{CN}$ (10)
(78) <sup>e</sup>	8.2	86s	0.4	78	$\tau_{NCH_3}$ (53), $\omega_{NH}$ (24)
(32) <sup>e</sup>	2.9	(32) <sup>e</sup>	0.1	32	$\tau_{CCH_3}$ (54), $\Pi_{CO}$ (21)

<sup>a</sup> s = symmetric stretch, as = asymmetric stretch, b = bend, sd = symmetric bend, ad = asymmetric bend, ob = out-of-plane bend, r = rocking,  $\tau$  = torsion.

<sup>b</sup> IR intensities in km/mole.

<sup>c</sup> Raman scattering activity in (a<sup>4</sup>)/amu.

<sup>d</sup> Unscaled frequencies.

<sup>e</sup> Calculated value.

<sup>f</sup> Raman spectral value from our work.

of the systematic error in the force constant matrix. In Table 3, the calculated and observed infrared and Raman frequencies and band intensities along with the assignment from potential energy distribution are given only for the most stable *trans* conformer of NMF with CH<sub>3</sub> group in staggered position for which all the eigen values were positive. The assign-

ments are made by matching the calculated frequencies and the infrared intensities with those observed in the spectra. The calculated frequencies are appropriate for isolated molecules where the intermolecular interactions are minimum. Therefore the calculated frequencies are compared with the spectra of matrix isolated species [29]. The assignments for NMF agree

Table 5

Comparison of the assignments (the value in the parenthesis represent potential energy distribution,  $\nu$ , stretching;  $\delta$ , bending;  $\Pi$ , out of plane bend;  $\tau$ , torsion) for the amide bands of NMF

	<i>trans</i>					<i>cis</i>	
	Expt [29] $\nu$ (cm <sup>-1</sup> )	ATT <sup>a</sup>	SH <sup>a</sup>	Suzuki <sup>a</sup>	Present	Present	Expt [29] $\nu$ (cm <sup>-1</sup> )
Amide I	1721	$\nu_{\text{CO}}(85)$	$\nu_{\text{CO}}(77)$	$\nu_{\text{CO}}(72)$ $\nu_{\text{CN}}(27)$	$\nu_{\text{CO}}(74)$ $\delta_{\text{CH}}(13)$	$\nu_{\text{CO}}(68)$ $\delta_{\text{CH}}(31)$	
Amide II	1528	$\delta_{\text{NH}}(57)$ $\nu_{\text{CN}}(26)$	$\delta_{\text{NH}}(49)$ $\nu_{\text{CN}}(20)$	$\delta_{\text{NH}}(75)$ $\nu_{\text{CO}}(16)$	$\delta_{\text{NH}}(51)$ $\nu_{\text{CN}}(22)$	$\delta_{\text{NH}}(31)$ $\delta_{\text{aCH}_3}(31)$	1448
CH bend	1392	$\delta_{\text{CH}}(88)$	$\delta_{\text{CH}}(77)$	$\delta_{\text{CH}}(60)$ $\nu_{\text{CN}}(32)$	$\delta_{\text{CH}}(56)$ $\delta_{\text{CO}}(33)$	$\nu_{\text{CN}}(48)$ $\delta_{\text{NH}}(22)$	
Amide III	1207	$\nu_{\text{CN}}(32)$ $\nu_{\text{NC}}(35)$	$\nu_{\text{CN}}(43)$ $\nu_{\text{NC}}(23)$	$\nu_{\text{CN}}(33)$ $\delta_{\text{CH}}(36)$	$\nu_{\text{CN}}(29)$ $\nu_{\text{NC}}(27)$ $\delta_{\text{NH}}(15)$	$\delta_{\text{CH}}(49)$ $\delta_{\text{CO}}(31)$	1302
Amide IV	761	$\delta_{\text{CO}}(63)$	$\delta_{\text{CO}}(55)$ $\delta_{\text{CNC}}(22)$	$\delta_{\text{CO}}(60)$ $\delta_{\text{CNC}}(18)$	$\delta_{\text{CO}}(42)$ $\delta_{\text{CNC}}(21)$	$\delta_{\text{CO}}(35)$ $\nu_{\text{NC}}(21)$ $\delta_{\text{CNC}}(14)$	
Amide V	880	$\Pi_{\text{CH}}(100)$	$\Pi_{\text{CH}}(98)$	$\Pi_{\text{CH}}(85)$	$\Pi_{\text{CH}}(95)$	$\Pi_{\text{CH}}(94)$	
Amide VI	570	$\tau_{\text{CN}}(77)$ $\Pi_{\text{NH}}(44)$	$\Pi_{\text{NH}}(69)$	$\Pi_{\text{NH}}(54)$ $\tau_{\text{CN}}(34)$	$\tau_{\text{CN}}(82)$	$\tau_{\text{CN}}(61)$ $\Pi_{\text{NH}}(29)$	629
Amide VII	368	$\Pi_{\text{NH}}(58)$ $\tau_{\text{CN}}(24)$	$\tau_{\text{CN}}(53)$	$\tau_{\text{CN}}(57)$ $\Pi_{\text{NH}}(42)$	$\Pi_{\text{NH}}(96)$	$\tau_{\text{CN}}(36)$ $\Pi_{\text{NH}}(28)$	195

<sup>a</sup> ATT = Ataka et al. [29]; SH = Sugawara et al. [4]; Suzuki [28].

with those of Ataka et al. [29] and hence they are not discussed further. It is satisfying to note that the calculated infrared intensities too agree qualitatively with the observed intensities for the matrix-isolated species.

The vibrational spectra of NMA have been of continued interest since the first paper of Miyazawa et al. [30] in 1958 who performed a partial normal co-ordinate analysis. As pointed out previously, ab initio molecular orbital calculations have been performed at the HF and MP2 level using different basis sets and the calculations have yielded at least one negative eigen value [7–12]. However, the present calculations have shown that the *cis-trans* conformer of *trans*-NMA represents the global minima for which the eigen values are all positive. The calculated and observed frequencies and band intensities along with their assignment from potential energy distribution are given in Table 4. Here too the calculated infrared band intensities are in agreement with those observed qualitatively, for the matrix isolated spectra [29].

Some differences exist regarding the assignment of the low frequency out of plane ( $a''$ ) modes of NMA observed at 619, 439 and 199 cm<sup>-1</sup>. The Raman spectrum of NMA in the liquid phase show a weak band at 199 cm<sup>-1</sup> and it could be attributed to NH out-of-plane bending in agreement with Mirkin and Krimm [10,11].

The observed qualitative band intensities from Raman spectra for the liquid sample differ from those calculated particularly for NMF. In the condensed phase the intensities of the bands may differ from those in the vapor phase due to hydrogen bonding. The ab initio calculations generally reproduce infrared intensities relatively in better agreement with the experiment. However, the calculated Raman intensities for NMA are qualitatively in better agreement with the experiment.

The infrared spectra of NMF in liquid state exhibits strong bands at 771, 1150, 1384 cm<sup>-1</sup>, etc., while the corresponding bands are of very weak intensity in the matrix isolated spectra. It shows that the intensity of

Table 6

Comparison of the assignments (s = symmetric stretch, as = asymmetric stretch, b = bend, sd = symmetric bend, ad = asymmetric bend, ob = out-of-plane bend, r = rocking,  $\tau$  = torsion) for the amide bands of NMA

	<i>trans</i>					<i>cis</i>	
	Expt [29] ( $\text{cm}^{-1}$ )	ATT <sup>a</sup>	SH <sup>a</sup>	MK <sup>a</sup>	Present	Present	Expt [29] ( $\text{cm}^{-1}$ )
Amide I	1707	$\nu_{\text{CO}}(86)$	$\nu_{\text{CO}}(79)$	$\nu_{\text{CO}}(83)$	$\nu_{\text{CO}}(77)$	$\nu_{\text{CO}}(73)$	1707
Amide II	1511	$\delta_{\text{NH}}(48)$	$\delta_{\text{NH}}(47)$	$\delta_{\text{NH}}(44)$	$\nu_{\text{NH}}(47)$	$\delta_{\text{NH}}(49)$	1432
		$\nu_{\text{CN}}(31)$	$\nu_{\text{CN}}(23)$	$\nu_{\text{CO}}(33)$	$\nu_{\text{CN}}(27)$	$\nu_{\text{CN}}(15)$	
Amide III	1266	$\nu_{\text{CN}}(25)$	$\nu_{\text{CN}}(35)$	$\delta_{\text{NH}}(26)$	$\nu_{\text{CN}}(28)$	$\nu_{\text{CN}}(28)$	825
		$\delta_{\text{CO}}(31)$	$\delta_{\text{CO}}(18)$	$\delta_{\text{CH}}(20)$	$\delta_{\text{NH}}(23)$	$\delta_{\text{CH}_3}(20)$	
		$\delta_{\text{NH}}(19)$	$\delta_{\text{NH}}(18)$	$\nu_{\text{CN}}(15)$	$\delta_{\text{CO}}(13)$	$\delta_{\text{CO}}(13)$	
Amide IV	761	$\delta_{\text{CO}}(63)$	$\delta_{\text{CO}}(39)$	$\nu_{\text{CC}}(37)$	$\delta_{\text{CO}}(40)$	$\delta_{\text{CO}}(38)$	510
		$\nu_{\text{CC}}(32)$	$\nu_{\text{CC}}(31)$	$\delta_{\text{CO}}(36)$	$\nu_{\text{CC}}(33)$	$\delta_{\text{NCC}}(28)$	
Amide V	619	$\tau_{\text{CN}}(39)$	$\Pi_{\text{CO}}(76)$	$\Pi_{\text{CO}}(68)$	$\Pi_{\text{CO}}(68)$	$\Pi_{\text{CO}}(63)$	619
		$\Pi_{\text{NH}}(37)$	$r_{\text{CH}_3}(26)$	$r_{\text{CH}_3}(30)$	$\omega_{\text{CH}_3}(24)$		
Amide VI	391	$\Pi_{\text{CO}}(88)$	$\tau_{\text{CN}}(107)$	$\tau_{\text{CN}}(109)$	$\tau_{\text{CN}}(55)$	$\tau_{\text{CN}}(45)$	510
	439		$\Pi_{\text{NH}}(59)$	$\Pi_{\text{NH}}(68)$	$\Pi_{\text{NH}}(28)$	$\Pi_{\text{NH}}(23)$	
Amide VII	175	$\tau_{\text{CN}}(63)$	$\Pi_{\text{NH}}(67)$	$\Pi_{\text{NH}}(84)$	$\Pi_{\text{NH}}(81)$	$\tau_{\text{NCH}_3}(35)$	195
				$\tau_{\text{CN}}(14)$	$\tau_{\text{CN}}(10)$	$\tau_{\text{CN}}(21)$	

<sup>a</sup> ATT = Akata et al. [29]; SH = Sugawara et al. [8]; MK = Mirkin and Krimm [10,11].

the bands change drastically from the matrix isolated spectra to liquid phase spectra. Similarly the infrared spectrum of NMA (liquid) shows strong bands at 600, 620, 1151, 993  $\text{cm}^{-1}$ , etc. The bands in the spectra of NMF and NMA are shifted considerably in the liquid phase compared to those in the vapor due to strong hydrogen bonding in the liquid.

A comparison of the assignments of the amide bands of NMF and NMA made by different authors are given in Tables 5 and 6, respectively. Tables 5 and 6 reflect the changes expected for *cis* isomers of NMF and NMA from those of the corresponding *trans* isomers for the amide bands. It also reflects the effect of basis sets and hence of different force constants employed. In the case of NMF, the assignment of Suzuki [28] is significantly different for the amide III band. The assignments for the two low frequency bands, amide VI and amide VII are also different. Significant differences in the amide bands between the *cis* and *trans* isomers of NMF lie in the lowering of NH, CH and CO bending frequencies and increase in the C–N stretching frequency in the *cis* form. However, the out of plane skeletal modes show different behavior. While the CN torsional frequency shows

an increase, the NH bending frequency shows a decrease in the *cis* compound. Some changes are also observed in the nature of vibrations. In the case of NMA, the contribution of CN stretching to amide III band is significantly low. Regarding amide V and VI bands, the assignment of Ataka et al. [29] is not consistent with those of Sugawara et al. [8], Mirkin and Krimm [9–12] and also the present work. Their assignment possibly should be revised for these two bands. The assignment of Ataka et al. [29] is also somewhat different for CN torsion.

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