



<http://www.orientjchem.org>

ISSN: 0970-020 X; CODEN: OJCHEG
Oriental Journal of Chemistry
2011, Vol. 27, No. (1): Pg. 271-275

Vibrational Spectroscopic Studies and Ab initio Calculations of N-methylacetamide

SHEENA MARY Y.¹, LINDA JACOB²,
HEMA TRESA VARGHESE¹ and C.YOHANNAN PANICKER³

¹Department of Physics, Fatima Mata National College, Kollam, Kerala (India).

²Department of Physics, Catholicate College, Pathanamthitta, Kerala (India).

³Department of Physics, TKM College of Arts and Science, Kollam, Kerala, (India).

(Received: December 14, 2010; Accepted: February 11, 2011)

ABSTRACT

Fourier-transform-Raman and infrared spectrum of N-methylacetamide were recorded and analyzed. The vibrational wavenumbers were examined theoretically using the Gaussian03 set of quantum chemistry codes. The first hyperpolarizability, predicted infrared intensities and Raman activities are reported. The calculated first hyperpolarizability makes this compound an attractive object for future studies of nonlinear optics. The experimental frequencies are in agreement with the calculated scaled values.

Key words: FT-Raman, FT-IR, HF calculations, Acetamide.

INTRODUCTION

Spectroscopic investigation of N-methylacetamide(NMA), which is considered a model for a peptide bond in proteins, can provide information about secondary structure of proteins in the gas phase as well as in solution. Numerous Infrared and Raman experiments have focused on the spectral region spanned by the three amide bands of NMA¹⁻⁸ particularly in the easily dictable amide I regime that overlaps with the carbon-oxygen stretch. In liquid water, carbon-oxygen stretch responds to the presence of water molecules by forming hydrogen bonds, and the resulting frequency shift can be used to assess the dynamics

of protein-solvent interactions. Similarly the amide II and amide III bands, which overlap with the NH in-plane wagging motion, can be used to describe the interaction between CO and NH, which are the backbone of a protein. And since the amide hydrogen can form a bond with the solvent, that is H₂O...NH, corresponding frequency shifts provide further information on protein behavior in aqueous solution. Senthil kumar *et al.*⁹ studied electron density and energy decomposition analysis in hydrogen bonding complex of azabenzenes with water, acetamide and thioacetamide have been carried out to explore the controversy involved in the relative order of their stability in a systematic way. Jong *et al.*¹⁰ have studied experimentally the

hydrogen bonding ability of azabenzene and methyl substituted azabenzene with thioacetamide, acetamide and water and concluded that the order of proton affinity is not same as those of the corresponding standard enthalpy. In the present study the IR, Raman and theoretical calculations of the frequencies for N-methylacetamide are reported.

EXPERIMENTAL

The FT-IR spectrum was recorded using a Perkin-Elmer FT-IR spectrometer. The spectral resolution was 4 cm⁻¹. Standard KBr was used. The FT-Raman spectrum was obtained on a Bruker IFS 66V NIR-FT instrument equipped with a FRA 106 Raman module. An Nd/YAG laser at 1064 nm with an output on 300mw was used as the exciting source.

Computational details

Calculations of N-methylacetamide are carried out with Gaussian 03 program¹¹ using the Hartree-Fock/631G* basis set to predict the molecular structure and vibrational wave numbers. Molecular geometry was fully optimized by Berny's optimization algorithm using redundant internal coordinates. Harmonic vibrational wave numbers are

calculated using the analytic second derivatives to confirm the convergence to minima on the potential surface. The wave number values computed at the HF level contain known systematic errors due to the negligence of electron correlation¹², and we hence used the scaling factor value of 0.8929 for HF/6-31G* basis set. Parameters corresponding to optimized geometry of N-methylacetamide (Figure 1) is given in table 1. The absence of imaginary wave numbers on the calculated vibrational spectrum confirms that the structure deduced corresponds to minimum energy.

RESULTS AND DISCUSSION

The observed Raman and IR bands with their relative intensities, calculated values and assignments are given in Table 2.

The observed IR bands with their relative intensities and calculated wave numbers and assignments are given in table. The NH stretching vibrations^{13,14} generally give rise to bands at 3500-3300 cm⁻¹. In the present study, the NH stretching band has split in to a doublet 3294, 3100 cm⁻¹ in the IR spectrum owing to the Davydov coupling between neighboring units. A similar type of splitting observed

Table 1: Optimized geometrical parameters of the title compound

Bond Lengths (Å)		Bond angles (°)		Dihedral angles (°)	
C ₁ -C ₂	1.5056	C2-C1-N3	116.5	D(3,1,2,5)	-151.2
C ₁ -N ₃	1.3524	C2-C1-O4	121.7	D(3,1,2,6)	-29.6
C ₁ -O ₄	1.2294	N3-C1-O4	121.7	D(3,1,2,7)	90.9
C ₂ -H ₅	1.0791	C1-C2-H5	109.0	D(4,1,2,5)	30.2
C ₂ -H ₆	1.0822	C1-C2-H6	112.5	D(4,1,2,6)	151.8
C ₂ -H ₇	1.0844	C1-C2-H7	109.4	D(4,1,2,7)	-87.6
N ₃ -H ₈	0.9903	H5-C2-H6	109.4	D(2,1,3,8)	1.3
C ₉ -N ₃	1.4535	H5-C2-H7	108.0	D(2,1,3,9)	-178.1
C ₉ -H ₁₀	1.0808	H6-C2-H7	108.4	D(4,1,3,8)	179.8
C ₉ -H ₁₁	1.0801	C1-N3-H8	119.6	D(4,1,3,9)	0.5
C ₉ -H ₁₂	1.0815	C1-N3-C9	121.6	D(1,3,9,10)	-57.4
		H8-N3-C9	118.8	D(1,3,9,11)	-117.3
		N3-C9-H10	110.7	D(1,3,9,12)	62.7
		N3-C9-H11	108.8	D(8,3,9,10)	123.2
		N3-C9-H12	111.0	D(8,3,9,11)	3.3
		H10-C9-H11	109.1	D(8,3,9,12)	-116.7
		H10-C9-H12	108.1		
		H11-C9-H12	109.0		

in acetanilide^{15,16} and N-methyl acetamide¹⁷ in the stretching band is attributed to the Davydov splitting. The splitting of about 194 cm⁻¹ in the IR spectrum is due to strong inter molecular hydrogen bonding. Further more, the N-H stretching wave number is red-shifted by 204 cm⁻¹ in the IR spectrum with a strong intensity from the computed wave number, which indicates the weakening of the N-H bond resulting in proton transfer¹⁸ to the neighboring oxygen atom O₄. In N-mono substituted amides, the in-plane bending frequency and the resonance

stiffened C-N bond stretching frequency fall close together and therefore interact. The CNH vibration where the nitrogen and hydrogen move in opposite direction relative to the carbon atom involves both NH bending and C-N stretching and absorbs¹⁹ strongly near 1550 cm⁻¹. This band is very characteristic for mono substituted amides. The CNH vibration where the N and H atoms move in the same direction relative to the carbon atom gives rise¹⁹ to a weaker band near 1250 cm⁻¹. In the present case the bands observed at 1563, 1299 cm⁻¹

Table 2: Infrared, Raman spectral data and calculated wave numbers and band assignments for N-methyl acetamide

					Assignments
3498	42.02	49.23	3294	3329	ν NH
2965	8.42	64.90	-	-	ν_{as} CH ₃
2950	26.00	70.83	-	-	ν_{as} CH ₃
2936	32.95	54.64	2946	2936	ν_{as} CH ₃
2925	18.59	62.64	-	-	ν_{as} CH ₃
2872	37.62	115.38	2900	-	ν_s CH ₃
2864	8.09	116.92	-	-	ν_s CH ₃
1658	248.28	3.58	1655	1663	ν C=O
1529	288.20	11.42	1563	-	δ NH
1493	9.51	9.33	-	-	δ_{as} CH ₃
1469	17.86	6.02	-	-	δ_{as} CH ₃
1468	2.70	34.41	-	1470	δ_{as} CH ₃
1452	4.13	10.55	-	-	δ_{as} CH ₃
1445	52.87	13.21	-	-	δ_s CH ₃
1406	33.91	3.98	1412	1417	δ_s CH ₃
1285	119.19	2.30	1299	1306	δ NH
1178	4.51	6.42	1151	1163	ρ CH ₃
1141	1.65	4.03	-	-	ρ CH ₃
1080	15.58	1.97	1096	1001	ρ CH ₃
1069	16.20	1.02	1042	-	ρ CH ₃
979	14.53	1.72	991	990	ν C-C
849	3.76	9.57	881	865	ν CN
618	17.76	5.86	629	630	γ NH
595	22.01	4.79	599	-	γ C=O
521	157.06	0.60	-	-	γ C=O
412	11.63	1.08	440	441	τ C=O
256	8.62	0.45	-	290	τ CH ₃
184	5.30	0.14	-	-	τ CH ₃
50	1.16	0.28	-	-	τ NH
37	1.00	0.59	-	-	τ NH

ν -stretching; ω wagging; δ -in-plane deformation ; γ -out-of-plane deformation; ρ -rocking ; τ -twisting; t -torsional; subscript: as-asymmetric; s-symmetric.

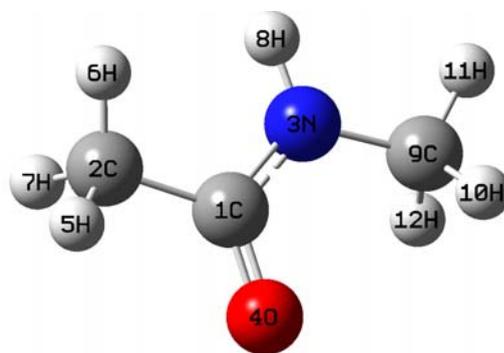
¹ in the IR spectrum and 1306 cm⁻¹ in the Raman spectrum and at 1529, 1285 cm⁻¹ (HF) are assigned as CNH bending modes. The out-of-plane NH wag absorbs at 629 cm⁻¹ in the IR spectrum and at 630 cm⁻¹ in Raman spectrum and theoretically at 618 cm⁻¹.

In aromatic compounds, the asymmetric stretching vibrations^{19,20} of CH₃ are expected in the range of 2905-3000 cm⁻¹ and symmetric CH₃ vibrations in the range of 2860-2870 cm⁻¹. The first of these results from the anti symmetric stretching $\nu_{as}CH_3$ mode in which two C-H bonds of the methyl group are extending while the third one is contracting. The second arises from the symmetrical stretching ν_sCH_3 in which all three of the C-H bonds extend and contract in phase. The asymmetric stretching modes of the methyl group are calculated to be 2965, 2950, 2936 and 2925 cm⁻¹ and the symmetric mode at 2872, 2864 cm⁻¹. The bands observed at 2946 and 2900 cm⁻¹ in the IR spectrum are assigned as asymmetric and symmetric methyl modes, respectively. The band observed 2936 cm⁻¹ in the Raman spectrum is assigned as $\nu_{as}CH_3$. Two bendings can occur within a methyl group. The first of these, the symmetrical bending vibration, involves the in-phase bending of the C-H bonds. The second, the anti symmetrical bending vibration, involves out-of-phase bending of the C-H bonds. The asymmetrical deformations are expected in the range²⁰ 1400-1485 cm⁻¹. The calculated values of $\delta_{as}CH_3$ modes are at 1493, 1469, 1468, 1452 cm⁻¹ and no bands are observed in the IR spectrum. In many molecules, the symmetric deformation δ_sCH_3 appears with an intensity varying from medium to strong and expected in the region 1380 ± 25 cm⁻¹. In this case δ_sCH_3 is calculated at 1445, 1406 cm⁻¹ theoretically and the band at 1412 in the IR spectrum, 1417 cm⁻¹ in Raman spectrum are assigned as these modes²⁰. The rocking modes of CH₃ are expected in the region²⁰ 900-1200 cm⁻¹. In the present case ρCH_3 modes are calculated at 1178, 1141, 1080, 1069 cm⁻¹. The bands observed at 1151, 1096, 1042 in the IR spectrum and at 1163 cm⁻¹ in the Raman spectrum are assigned as rocking modes of the methyl group. The methyl torsion, often assigned²⁰ below 400 cm⁻¹.

The carbonyl group vibration gives rise to characteristic bands in vibrational spectra. The

intensity of these bands can increase owing to the conjugation or formation of hydrogen bonds. The increase in conjugation, therefore, leads to identification of IR bands. The carbonyl absorption²¹ $\nu C=O$ of one membered ring occurs in the region 1658 cm⁻¹ and in the present case, this band is observed in the IR spectrum at 1655 cm⁻¹ and at 1663 cm⁻¹ in the Raman spectrum and the theoretical value is at 1658 cm⁻¹. The deformation bands of the C=O are also identified at 599 cm⁻¹ in the IR spectrum and at 595, 521 cm⁻¹ theoretically²⁰.

The νCC is identified at 979 cm⁻¹ theoretically and at 991 in the IR spectrum and at 990 cm⁻¹ in the Raman spectrum. The νCN is identified in 849 (HF) and the observed bands are at 881 cm⁻¹ (IR) and 865 cm⁻¹ (Raman). The torsional vibrations are observed below 500 cm⁻¹.



For the title compound the bond length C₁-O₄=1.2294Å and this value is in agreement with the reported value 1.203Å, 1.2074Å^{22,23}. The bond lengths, C₁-C₂=1.5056Å, is in agreement with the reported value 1.526Å and 1.522Å^{22,23}. The bond lengths of C₂-H₅=1.0791, C₂-H₆=1.0822, C₂-H₅=1.0844, C₉-H₁₀=1.0808, C₉-H₁₁=1.0801, C₉-H₁₂=1.0815Å and these values are in agreement with the reported values 1.081, 1.071Å^{22,23}. Purkayastha and Chattopadhyay²⁴ reported C₁-N₃, C₉-N₃ bond lengths as 1.3270, 1.4Å for benzothiazole and 1.3503, 1.407Å for benzimidazole compounds. For the title compound the corresponding values are 1.3524 and 1.4535Å. At C₁ the bond angles are (C₂-C₁-N₃, C₂-C₁-O₄, N₃-C₁-O₄) 116.5, 121.7, 121.7 and the deviation from 120° shows that the interaction between CH₃ and NH group. The C-C and C-H bond lengths are in agreement with the reported values^{25,26}. The calculated first hyperpolarizability of

the title compound is 0.467×10^{-30} esu and is an attractive object for future studies of nonlinear optics.

CONCLUSION

The IR and Raman spectrum of N-methylacetamide were recorded and analysed. The

frequencies are calculated theoretically using Gaussian03 software package. The calculated frequencies are found to be in agreement with the experimental values. The geometrical parameters of the title compound are in agreement with the reported values of similar compounds.

REFERENCES

- Ataka, S., Takeuchi, H., and Tasumi, M.J., *J. Mol. Struct.* **113**: 147 (1984).
- Mayne, L.C., and Hudson, B.J., *Phys. Chem.* **95**: 2962 (1991).
- Chen, X.G., Stenner, R.S., Asher, S.A., Mirkin, N.G., and Krimms, S.J., *Phys. Chem.* **99**: 3074 (1995).
- Torri, H., Tasumi, T., and Tasumi, M.J., *J. Raman Spectrosc.* **29**: 537 (1998).
- Kubelka, J., and Keiderling, A.J., *Phys. Chem. A* **105**: 10922 (2001).
- Cueval, G., Krishnan, R., Madrid, G., and Hagler, A.T., *Phys. Chem.* **4**: 1490 (2002).
- Papamokar, G.V., and Demetropoulos, I.N.J., *Phys. Chem. A* **108**: 7291 (2004).
- Zhang, R., Li, H.R., Lei, Y., and Han, S.J.J., *J. Mol. Struct.* **693** : 17 (2004).
- Senthikumar, L., Ghanty, T.K., and Crhosh, S.K., *J. Phys. Chem. A* **109**: 7575 (2005).
- Jong, H.M., Lei, J., Kun-Jung, K., Hee, J.J., Young-Sang, C., Jeicnghec, P., and Chang-Ju, Y.J., *Phys. Chem. A* **108**: 921 (2004).
- Frisch, M.J., et al. *Gaussian03, Revision C.02*, Gaussian, Inc., Wallingford CT (2004).
- Foresman, J.B., and Frisch, E., in: *Exploring Chemistry with Electronic Structure Methods: A Guide to using Gaussian*, Gaussian Pittsburg, PA (1996).
- Bellamy, L.J., *The IR spectra of complex molecules*, John Wiley and Sons, New York (1975).
- Spire, A., Barthes, M., Hallouai, H., and De Nunzio, G., *Physics D* **137**: 392 (2000).
- Edler, J., Pfister, R., Pouthier, V., Falvo, C., and Hamm, P., *Phys. Rev. Lett.* **93**: 106405 (2004).
- Edler, J., Hamm, P., and Scott, A.C., *Phys. Rev. Lett.* **88**: 067403 (2002).
- Edler, J., and Hamm, P., *Phys. Rev.*, **B69**: 214301 (2004).
- Barthes, M., DeNunzio, G., and Ribet, G., *Synth. Met.* **76**: 337 (1996).
- Colthup, N.B., Daly, L.H., and Wiberly, S.E., *Introduction to Infra red and Raman Spectroscopy*, Academic Press, New York (1975).
- Roeges, N.P.G., *A Guide to Complete Interpretation of Organic Structures*, Wiley New York (1994).
- Silverstein, R.M., Bassler, G.C., and Morill, T.C., *Spectrometric Identification of Organic Compounds*, 5th.ed. John Wiley and sons Inc. Singapore (1991).
- Naverette, J.T.L., Bencivenni, L., Ramondo, F., Hernandez, V., and Ramirez, F.J., *J. Mol. Struct. (Theochem)*, **330**: 261 (1995).
- Van Alsenoy, C., Kulp, S., Siam, K., Klimkowski, V.J., Whank, J.D.E., and Schafer, L., *J. Mol. Struct. (Theochem)*, **181**: 169 (1998).
- Purkayastha, P., and Chattopadhyay, N., *Phys. Chem. Phys.* **2**: 303 (2003).
- Lijima, K., Tanaka, K., and Onuma, S., *J. Mol. Struct.* **246**: 257 (1991).
- Lijma, K., and Beagley, B., *J. Mol. Struct.* **248**: 133 (1991).