Vibrational Analysis of Peptides, Polypeptides, and Proteins. X. Poly(glycine I) and Its Isotopic Derivatives

Anil M. Dwivedi and S. Krimm*

Biophysics Research Division, The University of Michigan, Ann Arbor, Michigan 48109.

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ABSTRACT: The normal modes of various isotopic species of poly(glycine I) in the antiparallel-chain rippled-sheet structure have been calculated, as a test of the force field for the parent polypeptide. In the light of these results, and to improve the prediction of some of the CH_2 modes as well as the transferability of the force field, some small modifications have been made to our previous force field.[5] This has resulted in a general improvement of predicted frequencies, particularly of CH_2 wag and CH_2 twist modes, and a very satisfactory accounting of the infrared bands of the isotopic molecules.

Introduction

The use of normal vibration calculations to provide reliable analyses of the infrared and Raman spectra of polypeptides, and thereby of related peptide and protein systems, depends on developing a force field with maximum transferability between different molecules. We have approached this problem by first analyzing simple peptide molecules[1,2] and then extending this force field to glycine polypeptides.[3,4] In the current series of studies our force field was further refined by using the spectra of poly(glycine I)[5] [(Gly I)$_n$] in the subsequently proposed[6] antiparallel-chain rippled-sheet (APRS) structure, β-poly(L-alanine)[7] [β-(Ala)$_n$] and β-poly(L-alanylglycine)[7] [β-(Ala-Gly)$_n$] in their known[8] antiparallel-chain pleated-sheet (APPS) structure, and α-poly(L-alanine).[9] This force field, together with our proposed transition dipole coupling mechanism,[10,11] has proved successful in predicting the characteristic modes of general β turns[12,13] as well as the amide modes of specific β-turn structures in proteins[14] and peptides.[15,16]

Since it is not possible at this stage to define a unique force field for as complex a molecule as a polypeptide, it is important to test the adopted force field on as many independent structures as feasible in order to substantiate its validity. One way of doing this is, as indicated above, to transfer it to other molecules. Another is to apply it to isotopic derivatives of a given molecule. We had done this previously[3] for (Gly I)$_n$ and its deuterated derivatives, but this was based on the (now known to be) incorrect APPS structure. We have now extended our calculations to APRS structures of isotopic derivatives of (Gly I)$_n$ for which infrared spectra are available[17] and, in addition, have obtained and analyzed the spectrum of N-deuterated β-poly(L-alanine) [β-(Ala-ND)$_n$].[18]

As a result of these combined studies on the deuterated derivatives of (Gly I)$_n$ and β-(Ala)$_n$, we have made some changes in force constants. In the present paper we report on the results for APRS (Gly I)$_n$, its three deuterated derivatives, and its ^{15}N derivative. In the accompanying paper[18] we give the results for β-(Ala)$_n$ and its N-deuterated derivative.

Table I
Internal and Local Symmetry Coordinates for One Chemical Repeat Unit of Crystalline Poly(glycine I)

A. Internal Coordinates[a]

$R_1 = \Delta r(\mathrm{C^{\alpha}{-}C})$
$R_2 = \Delta r(\mathrm{C{-}N})$
$R_3 = \Delta r(\mathrm{N{-}C^{\alpha}})$
$R_4 = \Delta r(\mathrm{C{=}O})$
$R_5 = \Delta r(\mathrm{N{-}H})$
$R_6 = \Delta r(\mathrm{C^{\alpha}{-}H})$
$R_7 = \Delta r(\mathrm{C^{\alpha}{-}H^{\alpha}})$
$R_8 = \Delta r(\mathrm{H\cdots O})$
$R_9 = \Delta r(\mathrm{H^{\alpha}\cdots H^{\alpha}})$
$R_{10} = \Delta\theta(\mathrm{C^{\alpha}{-}C{-}N})$
$R_{11} = \Delta\theta(\mathrm{C{-}N{-}C^{\alpha}})$
$R_{12} = \Delta\theta(\mathrm{N{-}C^{\alpha}{-}C})$
$R_{13} = \Delta\theta(\mathrm{C^{\alpha}{-}C{=}O})$
$R_{14} = \Delta\theta(\mathrm{N{-}C{=}O})$
$R_{15} = \Delta\theta(\mathrm{C{-}N{-}H})$
$R_{16} = \Delta\theta(\mathrm{C^{\alpha}{-}N{-}H})$
$R_{17} = \Delta\theta(\mathrm{N{-}C^{\alpha}{-}H})$
$R_{18} = \Delta\theta(\mathrm{N{-}C^{\alpha}{-}H^{\alpha}})$
$R_{19} = \Delta\theta(\mathrm{C{-}C^{\alpha}{-}H})$
$R_{20} = \Delta\theta(\mathrm{C{-}C^{\alpha}{-}H^{\alpha}})$
$R_{21} = \Delta\theta(\mathrm{H{-}C^{\alpha}{-}H^{\alpha}})$
$R_{22} = \Delta\theta(\mathrm{C{=}O\cdots H})$
$R_{23} = \Delta\theta(\mathrm{N{-}H\cdots O})$
$R_{24} = \Delta\omega(\mathrm{C{=}O})$
$R_{25} = \Delta\omega(\mathrm{N{-}H})$
$R_{26} = \Delta\tau(\mathrm{C^{\alpha}{-}C})$
$R_{27} = \Delta\tau(\mathrm{C{-}N})$
$R_{28} = \Delta\tau(\mathrm{N{-}C^{\alpha}})$
$R_{29} = \Delta\tau(\mathrm{C{=}O\cdots H})$
$R_{30} = \Delta\tau(\mathrm{N{-}H\cdots O})$

B. Local Symmetry Coordinates

$S_1 = R_3$	N—C$^{\alpha}$ stretch
$S_2 = R_1$	C$^{\alpha}$—C stretch
$S_3 = R_2$	C—N stretch
$S_4 = R_4$	C=O stretch
$S_5 = R_5$	N—H stretch
$S_6 = R_6 + R_7$	CH_2 symmetric stretch
$S_7 = R_6 - R_7$	CH_2 antisymmetric stretch
$S_8 = R_8$	H···O stretch
$S_9 = R_9$	H$^{\alpha}$···H$^{\alpha}$ stretch
$S_{10} = 2R_{11} - R_{15} - R_{16}$	CNC$^{\alpha}$ deformation
$S_{11} = 5R_{12} - R_{17} - R_{18} - R_{19} - R_{20} - R_{21}$	NC$^{\alpha}$C deformation
$S_{12} = 2R_{10} - R_{13} - R_{14}$	C$^{\alpha}$CN deformation
$S_{13} = R_{13} - R_{14}$	C=O in-plane bend
$S_{14} = R_{15} - R_{16}$	N—H in-plane bend
$S_{15} = R_{22}$	C=O···H in-plane bend
$S_{16} = R_{23}$	N—H···O in-plane bend
$S_{17} = 4R_{21} - R_{17} - R_{18} - R_{19} - R_{20}$	CH_2 bend
$S_{18} = R_{17} + R_{18} - R_{19} - R_{20}$	CH_2 wag
$S_{19} = R_{17} - R_{18} - R_{19} + R_{20}$	CH_2 twist
$S_{20} = R_{17} - R_{18} + R_{19} - R_{20}$	CH_2 rock
$S_{21} = R_{24}$	C=O out-of-plane bend
$S_{22} = R_{25}$	N—H out-of-plane bend
$S_{23} = R_{26}$	C$^{\alpha}$—C torsion
$S_{24} = R_{27}$	C—N torsion
$S_{25} = R_{28}$	N—C$^{\alpha}$ torsion
$S_{26} = R_{29}$	C=O···H torsion
$S_{27} = R_{30}$	N—H···O torsion

[a] Δr = bond stretch, $\Delta\theta$ = angle bend, $\Delta\omega$ = out-of-plane bend, $\Delta\tau$ = bond torsion.

Force Field Refinement

The APRS (Gly I)$_n$ structural parameters used in the present calculations are the same as those used by Moore and Krimm,[5] who have also given the symmetry species and selection rules for this structure. These show the following distribution of number and activity of the normal modes: $\mathrm{A_g}[\nu(0,0)^{5}]$-21, Raman; $\mathrm{A_u}[\nu(0,\pi)]$-20, infrared (∥); $\mathrm{B_g}[\nu(\pi,\pi)]$-21, Raman; $\mathrm{B_u}[\nu(\pi,0]$-19, infrared (⊥). The internal and local symmetry coordinates of one chemical repeat unit used in our calculations are given in Table I, where the definitions follow those used previously.[5] The unit cell of APRS (Gly I)$_n$ has four chemical repeat units,

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Table II
Force Constants for Crystalline Poly(glycine I)

force constant[a]	value[b]	force constant[a]	value[b]
1. *f*(NC$^{\alpha}$)	5.043	42. *f*(C$^{\alpha}$C,C$^{\alpha}$CO)	0.200
2. *f*(C$^{\alpha}$C)	4.409	43. *f*(C$^{\alpha}$C,NC$^{\alpha}$H) *f*(C$^{\alpha}$C,NC$^{\alpha}$H$^{\alpha}$)	0.026
3. *f*(CN)	6.415	44. *f*(C$^{\alpha}$C,CC$^{\alpha}$H) *f*(C$^{\alpha}$C,CC$^{\alpha}$H$^{\alpha}$)	0.205
4. *f*(CO)	9.882	45. *f*(CN,C$^{\alpha}$CN)	0.300
5. *f*(NH)	5.840	46. *f*(CN,CNC$^{\alpha}$)	0.300
6. *f*(C$^{\alpha}$H) *f*(C$^{\alpha}$H$^{\alpha}$)	4.564	47. *f*(CN,NCO)	0.200
7. *f*(H· · ·O)	0.125	48. *f*(CN,CNH)	0.294
8. *f*(H$^{\alpha}$· · ·H$^{\alpha}$)	0.0027	49. *f*(CO,C$^{\alpha}$CO)	0.450
9. *f*(NC$^{\alpha}$C)	0.819	50. *f*(CO,NCO)	0.450
10. *f*(C$^{\alpha}$CN)	1.400	51. *f*(CO,C$^{\alpha}$CN)	−0.150
11. *f*(CNC$^{\alpha}$)	0.687	52. *f*(NC$^{\alpha}$C,C$^{\alpha}$NH)	−0.100
12. *f*(NCO)	1.246	53. *f*(NC$^{\alpha}$C,NC$^{\alpha}$H) *f*(NC$^{\alpha}$C,NC$^{\alpha}$H$^{\alpha}$)	−0.031
13. *f*(NC$^{\alpha}$H) *f*(NC$^{\alpha}$H$^{\alpha}$)	0.715	54. *f*(NC$^{\alpha}$C,CO ob)	−0.0725
14. *f*(C$^{\alpha}$NH)	0.527	55. *f*(NC$^{\alpha}$C,NH ob)	0.1092
15. *f*(C$^{\alpha}$CO)	1.246	56. *f*(C$^{\alpha}$CN,CNH)	0.200
16. *f*(CC$^{\alpha}$H) *f*(CC$^{\alpha}$H$^{\alpha}$)	0.684	57. *f*(CNC$^{\alpha}$,C$^{\alpha}$NH)	−0.040
17. *f*(CNH)	0.527	58. *f*(NC$^{\alpha}$H,CC$^{\alpha}$H) *f*(NC$^{\alpha}$H$^{\alpha}$,CC$^{\alpha}$H$^{\alpha}$)	0.019
18. *f*(H$^{\alpha}$C$^{\alpha}$H)	0.584	59. *f*(NC$^{\alpha}$H,HC$^{\alpha}$H$^{\alpha}$) *f*(NC$^{\alpha}$H$^{\alpha}$,HC$^{\alpha}$H$^{\alpha}$)	0.0615
19. *f*(CO· · ·H ib)	0.010	60. *f*(NC$^{\alpha}$H$^{\alpha}$,NH ob)	0.1022
20. *f*(NH· · ·O ib)	0.0506	61. *f*(NC$^{\alpha}$H,NC$^{\alpha}$H$^{\alpha}$)	0.0463
21. *f*(CO ob)	0.587	62. *f*(NC$^{\alpha}$H,NH ob)	0.0456
22. *f*(NH ob)	0.129	63. *f*(C$^{\alpha}$CO,CC$^{\alpha}$H$^{\alpha}$)	0.150
23. *f*(NC$^{\alpha}$ t)	0.037	64. *f*(C$^{\alpha}$CO,CC$^{\alpha}$H)	0.100
24. *f*(C$^{\alpha}$C t)	0.037	65. *f*(NCO,CNH)	0.251
25. *f*(CN t)	0.680	66. *f*(C$^{\alpha}$NH,CNH)	0.0065
26. *f*(NH t)	0.0015	67. *f*(C$^{\alpha}$NH,NC$^{\alpha}$H$^{\alpha}$)	0.100
27. *f*(CO t)	0.001	68. *f*(C$^{\alpha}$NH,NC$^{\alpha}$H)	0.031
28. *f*(NC$^{\alpha}$,C$^{\alpha}$C)	0.300	69. *f*(CC$^{\alpha}$H,CC$^{\alpha}$H$^{\alpha}$)	−0.032
29. *f*(C$^{\alpha}$C,CN)	0.300	70. *f*(CC$^{\alpha}$H,HC$^{\alpha}$H$^{\alpha}$) *f*(CC$^{\alpha}$H$^{\alpha}$,HC$^{\alpha}$H$^{\alpha}$)	0.0398
30. *f*(NC$^{\alpha}$,CN)	0.300	71. *f*(CC$^{\alpha}$H,CO ob) *f*(CC$^{\alpha}$H$^{\alpha}$,CO ob)	0.100
31. *f*(C$^{\alpha}$C,CO)	0.500	72. *f*(CO ob,NH ob)	0.010
32. *f*(CN,CO)	0.500	73. *f*(CO ob,CN t)	0.0111
33. *f*(C$^{\alpha}$H$^{\alpha}$,C$^{\alpha}$H)	0.010	74. *f*(NH ob,CN t)	−0.1677
34. *f*(C$^{\alpha}$H$^{\alpha}$,H$^{\alpha}$· · ·H$^{\alpha}$)	−0.0075	75. $F_{10,\mathrm{I}}$	0.102
35. *f*(NC$^{\alpha}$,CNC$^{\alpha}$)	0.300	76. $F_{01,\mathrm{I}}$	−0.244
36. *f*(NC$^{\alpha}$,NC$^{\alpha}$C)	0.300	77. $F_{11,\mathrm{I}}$	0.160
37. *f*(NC$^{\alpha}$,C$^{\alpha}$NH)	0.294	78. $F_{10,\mathrm{II}}$	−0.036
38. *f*(NC$^{\alpha}$,NC$^{\alpha}$H) *f*(NC$^{\alpha}$,NC$^{\alpha}$H$^{\alpha}$)	0.517	79. $F_{01,\mathrm{II}}$	−0.0095
39. *f*(NC$^{\alpha}$,CC$^{\alpha}$H) *f*(NC$^{\alpha}$,CC$^{\alpha}$H$^{\alpha}$)	0.026	80. $F_{11,\mathrm{II}}$	0.0091
40. *f*(C$^{\alpha}$C,NC$^{\alpha}$C)	0.300		
41. *f*(C$^{\alpha}$C,C$^{\alpha}$CN)	0.300		

[a] *f*(AB) = AB bond stretch, *f*(ABC) = ABC angle bend, *f*(X,Y) = XY interaction, *F* = transition dipole coupling;[10] ib = in-plane bend, ob = out-of-plane bend, t = torsion. [b] Units are mdyn/Å for stretch and stretch, stretch force constants, mdyn for stretch, bend force constants, and mdyn·Å for all others.

and their local symmetry coordinates are combined to give symmetry coordinates for each species in the same way as was done previously.[5]

The valence force field of Moore and Krimm[5] was used as a starting point for the present refinement. It was first tested on the isotopic molecules $-(NDCH_2CO)-_n$, $-(NHCD_2CO)-_n$, $-(NDCD_2CO)-_n$, and $-(^{15}NHCH_2CO)-_n$. For most of the modes the agreement was reasonable, but significant discrepancies were found for frequencies associated with CH_2 wag, CH_2 twist, CO out-of-plane bend, and the two Raman bands observed at 327 and 82 cm^{-1}. Before the actual refinement was started, a calculation was done for $-(NHCH_2CO)-_n$ in which all possible diagonal and off-diagonal force constants were included. The purpose of this was to obtain the detailed Jacobian matrix in order to determine which force constants were particularly important in influencing the above discrepancies. As a result we found it to be essential to include in the force field six new force constants: *f*(CNC$^{\alpha}$,C$^{\alpha}$NH), *f*(NC$^{\alpha}$C,NC$^{\alpha}$H), *f*(CNH,C$^{\alpha}$NH), *f*(C$^{\alpha}$H$^{\alpha}$,H$^{\alpha}$···H$^{\alpha}$), *f*(CO,C$^{\alpha}$CN), and *f*(C$^{\alpha}$H,C$^{\alpha}$H$^{\alpha}$). In addition, of the 13 force constants previously set equal to zero,[5] 4 were judged to be significant enough to be included in the refinement, viz., *f*(NC$^{\alpha}$C,NH ob), *f*(C$^{\alpha}$CO,CC$^{\alpha}$H$^{\alpha}$), *f*(NC$^{\alpha}$H,NH ob), and *f*(CC$^{\alpha}$H$^{\alpha}$,CO ob). In all, a total of 18 force constants were chosen to be modified in the least-squares refinement, using only infrared[17] and Raman[19] data on $-(NHCH_2CO)-_n$.

This refined force field gave quite reasonable results for all of the isotopic molecules. We next decided to transfer this force field to β-(Ala)$_n$, which, of course, has the APPS structure. When both (Gly I)$_n$ and β-(Ala)$_n$ were considered together, it was felt necessary to alter an additional 9 force constants for (Gly I)$_n$ in order to achieve maximum transferability of the force field. This alteration was accomplished manually.

A complete listing of the revised force field is given in Table II. Of the 80 nonzero force constants, 53 (including 6 for transition dipole coupling effects) are the same as reported earlier,[5] 21 are modified (including 4 which previously had zero values), and 6 are new force constants not included in the earlier force field. The NH stretching force constant was adjusted to make the calculated frequency agree with the unperturbed NH stretching frequency, found[5] at 3272 cm^{-1}. The only significant change in a

Table III
Observed and Calculated Frequencies (in cm^{-1}) of Poly(glycine I)

observed[a]		calculated				
Raman	IR	A_g	A_u	B_g	B_u	potential energy distribution[b]
						-(NHCH$_2$CO)-$_n$
		3272				NH s (98)
			3272			NH s (98)
				3271		NH s (98)
	3272 S[c]				3271	NH s (98)
2932 S		2934				CH$_2$ as (98)
2932 S				2934		CH$_2$ as (98)
	2929 W				2929	CH$_2$ as (99)
	2929 W		2928			CH$_2$ as (99)
2869 M		2865				CH$_2$ ss (98)
2869 M				2865		CH$_2$ ss (98)
	2869 VW		2861			CH$_2$ ss (99)
	2869 VW				2861	CH$_2$ ss (99)
				1695		CO s (77), CN s (15), C$^{\alpha}$CN d (11)
	1685 M		1689			CO s (75), CN s (20), C$^{\alpha}$CN d (11)
1674 S		1677				CO s (74), CN s (21), C$^{\alpha}$CN d (11)
	1636 S				1643	CO s (69), CN s (22), C$^{\alpha}$CN d (11)
				1602		NH ib (56), CN s (19), C$^{\alpha}$C s (12)
					1572	NH ib (51), C$^{\alpha}$C s (16), CN s (14)
	1517 S		1515			NH ib (35), CN s (28), C$^{\alpha}$C s (17), CO ib (14)
1515 W		1514				NH ib (35), CN s (27), C$^{\alpha}$C s (17), CO ib (14)
1460 S		1454				CH$_2$ b (66), CH$_2$ w (16)
			1454			CH$_2$ b (65), CH$_2$ w (17)
				1441		CH$_2$ b (96)
	1432 S				1439	CH$_2$ b (96)
1410 M		1415				CH$_2$ w (41), CH$_2$ b (31), NH ib (14)
	1408 W		1415			CH$_2$ w (40), CH$_2$ b (33), NH ib (13)
1341 W				1341		CH$_2$ w (84)
	1338 W				1338	CH$_2$ w (79)
				1304		NH ib (30), CO ib (19), CN s (18), C$^{\alpha}$C s (16)
	1295 W				1286	NH ib (39), C$^{\alpha}$C s (17), CO ib (16), CN s (12)
1255 M		1253				CH$_2$ tw (76), CH$_2$ w (17)
			1253			CH$_2$ tw (76), CH$_2$ w (17)
1234 S				1243		CH$_2$ tw (93)
	1236 M				1242	CH$_2$ tw (92)
1220 W		1213				NC$^{\alpha}$ s (29), NH ib (23), CH$_2$ w (18), CH$_2$ tw (16), CN s (13)
	1214 W		1212			NC$^{\alpha}$ s (29), NH ib (23), CH$_2$ w (18), CH$_2$ tw (15), CN s (13)
1162 M		1153				NC$^{\alpha}$ s (50), C$^{\alpha}$C s (13), NH ib (12)
			1152			NC$^{\alpha}$ s (50), C$^{\alpha}$C s (14), NH ib (12)
1021 VS				1015		NC$^{\alpha}$ s (77), C$^{\alpha}$C s (10)
	1016 M				1014	NC$^{\alpha}$ s (77), C$^{\alpha}$C s (10)
		1002				CH$_2$ r (45), CO s (11), C$^{\alpha}$C s (10)
			1000			CH$_2$ r (49), CO s (10)
	987 W				980	CH$_2$ r (68), CN s (10)
				979		CH$_2$ r (70), CN s (10)
		946				CH$_2$ r (29), CN s (12), C$^{\alpha}$C s (11), NC$^{\alpha}$C d (10)
	936 M		940			CH$_2$ r (25), CN s (13), C$^{\alpha}$C s (12), NC$^{\alpha}$C d (10)
	888 W				890	C$^{\alpha}$C s (29), CN s (21), CH$_2$ r (14), CO s (13)
884 M				890		C$^{\alpha}$C s (31), CN s (24), CO s (12), CH$_2$ r (12)
				768		CO ib (16), NC$^{\alpha}$ s (15), C$^{\alpha}$C s (15), CN t (12), NC$^{\alpha}$C d (11)
					767	C$^{\alpha}$C s (19), CO ib (17), NC$^{\alpha}$ s (16), NC$^{\alpha}$C d (11), CNC$^{\alpha}$ d (11)
				736		CN t (63), NH· · ·O ib (15), NH ob (11), H· · ·O s (11)
	708 S				718	CN t (75), NH· · ·O ib (19), NH ob (16), H· · ·O s (10)
			718			CN t (79), NH ob (26), NH· · ·O ib (23), H· · ·O s (10)
		702				CN t (79), NH ob (29), NH· · ·O ib (25), H· · ·O s (15)
		630				CO ib (36), CO ob (24), C$^{\alpha}$C s (10)
	628 W		629			CO ib (37), CO ob (23), C$^{\alpha}$C s (10)
	614 M				621	CO ob (67), C$^{\alpha}$CN d (15), NH ob (14), NC$^{\alpha}$C d (10)
				613		CO ob (59), C$^{\alpha}$CN d (20), NH ob (17), NC$^{\alpha}$C d (11)
					589	C$^{\alpha}$CN d (47), CO ob (17)
599 W				587		C$^{\alpha}$CN d (43), CO ob (24)
589 W		580				CO ob (45), CO ib (28), C$^{\alpha}$C s (12)
	589 M		579			CO ob (45), CO ib (27), C$^{\alpha}$C s (11)
327 W				323		NC$^{\alpha}$C d (21), CO ib (16), NH ob (15)
	321 W				320	NC$^{\alpha}$C d (21), CO ib (18), NH ob (15)
		291				C$^{\alpha}$CN d (51), NC$^{\alpha}$C d (21), NC$^{\alpha}$ s (10)
	285 W		290			C$^{\alpha}$CN d (56), NC$^{\alpha}$C d (19), NC$^{\alpha}$ s (12)
					252	CNC$^{\alpha}$ d (41), CO ib (28)
260 W				250		CNC$^{\alpha}$ d (41), CO ib (30), NH ob (15)
	217 W		226			CNC$^{\alpha}$ d (68), CO ib (10), H· · ·O s (10)
211 W		214				CNC$^{\alpha}$ d (74)
			180			NH ob (70), CO ob (20)
170 W		178				NH ob (67), CO ob (15), C$^{\alpha}$CN d (12), CH$_2$ w (12)
	140 M, br				140	H· · ·O s (46), CN t (46), NH ob (37), C$^{\alpha}$C t (11)

Table III (*Continued*)

observed^a		calculated				
Raman	IR	A$_g$	A$_u$	B$_g$	B$_u$	potential energy distribution^b
		135				H···O s (29), CN t (25), NC$^\alpha$C d (15)
112 M				111		H···O s (78), CN t (18)
			108			NC$^\alpha$C d (46), C$^\alpha$C t (16), NH ob (16), NC$^\alpha$ t (14)
82 S		88				NH ob (43), CN t (27), NC$^\alpha$C d (26), H$^\alpha$···H$^\alpha$ s (13), NC$^\alpha$ t (12), H···O s (11)
				71		C$^\alpha$C t (35), NC$^\alpha$ t (24), CN t (22), NH ob (22), NH···O ib (17)
			37			NH···O ib (38), CO···H ib (28), NH ob (18), H···O s (17)
				31		NH···O ib (35), CO···H ib (31), CN t (21), NH ob (16), NC$^\alpha$ t (13)
		12				NH t (52), CO t (34)
						-(NDCH$_2$CO)-$_n$
		2934				CH$_2$ as (98)
				2934		CH$_2$ as (98)
	2929 W				2929	CH$_2$ as (99)
	2929 W		2928			CH$_2$ as (99)
				2866		CH$_2$ ss (98)
		2865				CH$_2$ ss (98)
	2870 VW		2861			CH$_2$ ss (99)
	2870 VW				2861	CH$_2$ ss (99)
		2406				ND s (96)
			2406			ND s (96)
				2405		ND s (97)
	~2457 S^c				2405	ND s (97)
				1690		CO s (76), CN s (18), C$^\alpha$CN d (10)
	1680 M		1685			CO s (76), CN s (19), C$^\alpha$CN d (10)
		1673				CO s (75), CN s (21), C$^\alpha$CN d (10)
	1629 S				1639	CO s (68), CN s (23), C$^\alpha$CN d (10)
				1505		C$^\alpha$C s (27), CN s (21), ND ib (14), CO ib (13), CH$_2$ w (12), NC$^\alpha$ s (11), CH$_2$ b (11)
					1492	C$^\alpha$C s (29), CN s (15), CO s (14), CH$_2$ b (13), ND ib (12), CO ib (12), CH$_2$ w (11), NC$^\alpha$ s (10)
	1475 S		1486			C$^\alpha$C s (31), CN s (22), CH$_2$ w (17), CO ib (16)
		1485				C$^\alpha$C s (32), CN s (21), CH$_2$ w (17), CO ib (15)
		1441				CH$_2$ b (86)
			1441			CH$_2$ b (86)
				1429		CH$_2$ b (90)
	1432 S				1428	CH$_2$ b (87)
		1352				CH$_2$ w (69), NC$^\alpha$ s (16), CN s (14)
	1352 M		1352			CH$_2$ w (69), NC$^\alpha$ s (16), CN s (14)
				1335		CH$_2$ w (78)
					1334	CH$_2$ w (77), CN s (10)
		1249				CH$_2$ tw (93)
			1249			CH$_2$ tw (93)
				1243		CH$_2$ tw (92)
	1237 M				1242	CH$_2$ tw (92)
		1151				NC$^\alpha$ s (69), C$^\alpha$CN d (11)
			1151			NC$^\alpha$ s (69), C$^\alpha$CN d (11)
				1074		ND ib (55), CH$_2$ r (19), CO ib (11)
					1055	ND ib (49), CH$_2$ r (26), CO ib (10)
		1036				CH$_2$ r (23), ND ib (21), C$^\alpha$C s (19)
			1036			CH$_2$ r (23), ND ib (22), C$^\alpha$C s (19)
	1015 M				1006	NC$^\alpha$ s (78), C$^\alpha$C s (10)
				1006		NC$^\alpha$ s (78), C$^\alpha$C s (11)
	950 W		954			CH$_2$ r (50), ND ib (16), CO ob (11)
		953				CH$_2$ r (50), ND ib (16), CO ob (11)
				939		CH$_2$ r (58), ND ib (23)
					932	CH$_2$ r (49), ND ib (31)
		899				ND ib (38), CN s (20), CO s (11)
			892			ND ib (38), CN s (21), CO s (12)
					883	C$^\alpha$C s (29), CN s (25), CO s (13)
				882		C$^\alpha$C s (30), CN s (28), CO s (13)
					755	C$^\alpha$C s (20), CO ib (20), CNC$^\alpha$ d (15), NC$^\alpha$ s (14), NC$^\alpha$C d (11)
				754		CO ib (20), C$^\alpha$C s (19), CNC$^\alpha$ d (15), NC$^\alpha$ s (14), NC$^\alpha$C d (11)
				636		CO ob (69), CN t (14)
	625 W				627	CO ob (77)
		620				CO ob (32), CO ib (29), CH$_2$ r (10)
	614 W		620			CO ob (31), CO ib (29), CH$_2$ r (10)
	572 M		579			CO ob (38), CO ib (34), C$^\alpha$C s (13)
		578				CO ob (37), CO ib (36), C$^\alpha$C s (14)
					572	C$^\alpha$CN d (53)
				571		C$^\alpha$CN d (52), CO ob (10)
			522			CN t (72), ND ob (34), ND···O ib (23), D···O s (19)
				519		CN t (71), ND ob (37), ND···O ib (21), D···O s (14), CO ob (10)
	504 S				513	CN t (80), ND ob (34), ND···O ib (23), D···O s (14)
		506				CN t (82), ND ob (31), ND···O ib (26), D···O s (14)

Table III (*Continued*)

observed[a]		calculated				
Raman	IR	A$_g$	A$_u$	B$_g$	B$_u$	potential energy distribution[b]
				323		NC$^{\alpha}$C d (21), CO ib (16), ND ob (15)
					320	NC$^{\alpha}$C d (21), CO ib (17), ND ob (15)
		287				C$^{\alpha}$CN d (50), NC$^{\alpha}$C d (21), NC$^{\alpha}$ s (11)
			285			C$^{\alpha}$CN d (54), NC$^{\alpha}$C d (19), NC$^{\alpha}$ s (12)
					250	CNC$^{\alpha}$ d (41), CO ib (28), ND ob (11)
				247		CNC$^{\alpha}$ d (41), CO ib (30), ND ob (17)
			224			CNC$^{\alpha}$ d (68), CO ib (10), D···O s (10)
		212				CNC$^{\alpha}$ d (74)
			180			ND ob (68), CO ob (20)
		177				ND ob (64), CO ob (15), C$^{\alpha}$CN d (12), NC$^{\alpha}$ s (10), CH$_2$ w (10)
					139	D···O s (48), CN t (43), ND ob (35), C$^{\alpha}$C t (11)
		135				D···O s (29), CN t (25), NC$^{\alpha}$C d (15)
				111		D···O s (79), CN t (17)
			107			NC$^{\alpha}$C d (47), ND ob (17), C$^{\alpha}$C t (16) NC$^{\alpha}$ t (15)
		87				ND ob (43), CN t (27), NC$^{\alpha}$C d (27), H$^{\alpha}$···H$^{\alpha}$ s (13), NC$^{\alpha}$ t (12), D···O s (10)
				69		C$^{\alpha}$C t (35), NC$^{\alpha}$ t (25), ND ob (20), CN t (20), ND···O ib (17)
			36			ND···O ib (39), CO···D ib (28), ND ob (18), D···O s (17)
				31		ND···O ib (36), CO···D ib (31), CN t (21), ND ob (16), NC$^{\alpha}$ t (13)
		12				ND t (52), CO t (34)
						-(NHCD$_2$CO)-$_n$
		3272				NH s (98)
			3272			NH s (98)
				3271		NH s (98)
	3266 S[c]				3271	NH s (98)
				2193		CD$_2$ as (97)
		2191				CD$_2$ as (97)
	2165 W				2189	CD$_2$ as (97)
	2165 W		2187			CD$_2$ as (97)
		2100				CD$_2$ ss (95)
				2099		CD$_2$ ss (96)
	2118 W		2097			CD$_2$ ss (96)
	2118 W				2096	CD$_2$ ss (96)
				1687		CO s (80), CN s (13), C$^{\alpha}$CN d (11)
	1684 M		1681			CO s (78), CN s (20), C$^{\alpha}$CN d (11)
		1669				CO s (77), CN s (21), C$^{\alpha}$CN d (11)
	1627 S				1630	CO s (77), CN s (19), C$^{\alpha}$CN d (12)
				1588		NH ib (59), CN s (25), C$^{\alpha}$C s (10)
					1559	NH ib (53), CN s (23), C$^{\alpha}$C s (14), NC$^{\alpha}$ s (10)
	1498 S		1511			NH ib (40), CN s (30), CO ib (14), C$^{\alpha}$C s (14)
		1510				NH ib (40), CN s (29), CO ib (14), C$^{\alpha}$C s (14)
			1334			NH ib (40), C$^{\alpha}$C s (31), CD$_2$ w (16)
		1333				NH ib (41), C$^{\alpha}$C s (31), CD$_2$ w (16)
				1305		NH ib (36), C$^{\alpha}$C s (22), CO ib (17), CN s (15)
	1297 M				1285	NH ib (42), C$^{\alpha}$C s (20), CO ib (15), CN s (11)
		1186				NC$^{\alpha}$ s (70), CD$_2$ w (17)
	1189 M		1185			NC$^{\alpha}$ s (70), CD$_2$ w (17)
				1109		CD$_2$ w (37), CD$_2$ b (25), C$^{\alpha}$C s (15)
	1099 W				1108	CD$_2$ w (38), CD$_2$ b (25), C$^{\alpha}$C s (15)
		1074				CD$_2$ b (61)
	1073 W		1071			CD$_2$ b (65)
				1051		CD$_2$ b (60), CD$_2$ w (32)
					1050	CD$_2$ b (60), CD$_2$ w (32)
		1021				CD$_2$ b (27), CD$_2$ w (19), CN s (11)
	1015 W		1019			CD$_2$ b (23), CD$_2$ w (21), CN s (12)
					990	NC$^{\alpha}$ s (61), CN s (16)
				989		NC$^{\alpha}$ s (62), CN s (15)
				930		CD$_2$ tw (45), C$^{\alpha}$C s (11)
	928 W				929	CD$_2$ tw (42), C$^{\alpha}$C s (10)
		906				CD$_2$ tw (86)
			906			CD$_2$ tw (88)
					895	CD$_2$ tw (33), CN s (15), CD$_2$ r (12)
				892		CD$_2$ tw (30), CN s (17), CD$_2$ r (13)
		885				CD$_2$ w (27), CD$_2$ r (16), C$^{\alpha}$C s (10)
	866 W		883			CD$_2$ w (26), CD$_2$ r (18), C$^{\alpha}$C s (10)
		838				CD$_2$ r (34), CO ob (18), NH ob (11), CD$_2$ b (11)
			834			CD$_2$ r (33), CO ob (17), NH ob (10), CD$_2$ b (10)
				804		CD$_2$ r (45), C$^{\alpha}$C s (15), C$^{\alpha}$CN d (10)
					801	CD$_2$ r (49), C$^{\alpha}$C s (15), C$^{\alpha}$CN d (10)
				742		CN t (60), NH ob (21), NH···O ib (18), H···O s (14)
					728	CN t (56), NH ob (23), NH···O ib (19), H···O s (11)
	700 M		707			CN t (74), NH ob (22), NH···O ib (21), H···O s (18), CD$_2$ w (12)
		689				CN t (75), NH ob (23), NH···O ib (23), H···O s (14), CD$_2$ w (13)
				685		CO ib (14), C$^{\alpha}$C s (14), NC$^{\alpha}$C d (12), CD$_2$ r (12), CN t (12)

Table III (*Continued*)

observed[a]		calculated				
Raman	IR	A$_g$	A$_u$	B$_g$	B$_u$	potential energy distribution[b]
					681	CN t (24), CO ib (13), C$^\alpha$C s (12), NC$^\alpha$C d (11), CD$_2$ r (10)
					606	CO ob (62), C$^\alpha$CN d (15), NH ob (12), NC$^\alpha$C d (10)
		600				CO ib (54), C$^\alpha$C s (17)
	610 M		600			CO ib (55), C$^\alpha$C s (18)
				598		CO ob (58), C$^\alpha$CN d (18), NH ob (16)
	564 M				541	C$^\alpha$CN d (39), CD$_2$ w (22), CO ob (13)
				539		C$^\alpha$CN d (37), CD$_2$ w (22), CO ob (16)
		531				CO ob (50), CD$_2$ r (30)
	534 M		528			CO ob (49), CD$_2$ r (31)
				295		CO ib (33), NC$^\alpha$C d (26)
					294	CO ib (35), NC$^\alpha$C d (26)
			277			C$^\alpha$CN d (55), NC$^\alpha$C d (20), NC$^\alpha$ s (10)
		276				C$^\alpha$CN d (51), NC$^\alpha$C d (23)
					226	CNC$^\alpha$ d (34), NH ob (17), CO ib (11)
				226		CNC$^\alpha$ d (35), NH ob (24), CO ib (13)
			216			CNC$^\alpha$ d (67), CO ib (11)
		205				CNC$^\alpha$ d (75), CO ib (10)
			177			NH ob (70), CO ob (20), CD$_2$ w (11)
		175				NH ob (68), CO ob (16), CD$_2$ w (13), C$^\alpha$CN d (13), NC$^\alpha$ s (11)
					139	H···O s (47), CN t (46), NH ob (36), C$^\alpha$C t (11)
		133				H···O s (31), CN t (29), NC$^\alpha$C d (11)
				109		H···O s (78), CN t (18)
			101			NC$^\alpha$C d (42), C$^\alpha$C t (17), NC$^\alpha$ t (15), NH ob (14)
		80				NH ob (42), NC$^\alpha$C d (27), CN t (23), D$^\alpha$···D$^\alpha$ s (14), NC$^\alpha$ t (14)
				70		C$^\alpha$C t (35), NC$^\alpha$ t (25), CN t (22), NH ob (21), NH···O ib (16)
			35			NH···O ib (38), CO···H ib (28), NH ob (19), H···O s (16)
				31		NH···O ib (36), CO···H ib (31), CN t (22), NH ob (16), NC$^\alpha$ t (13)
		12				NH t (52), CO t (34)
						-(NDCD$_2$CO)-$_n$
		2407				ND s (96)
			2406			ND s (96)
				2405		ND s (97)
	~2458 S[c]				2405	ND s (97)
				2192		CD$_2$ as (97)
		2190				CD$_2$ as (97)
	2161 W				2189	CD$_2$ as (97)
	2161 W		2187			CD$_2$ as (97)
		2099				CD$_2$ ss (95)
				2099		CD$_2$ ss (96)
	2109 W		2096			CD$_2$ ss (96)
	2109 W				2095	CD$_2$ ss (96)
				1680		CO s (81), CN s (17), C$^\alpha$CN d (10)
	1681 M		1677			CO s (78), CN s (19), C$^\alpha$CN d (10)
		1665				CO s (77), CN s (20), C$^\alpha$CN d (10)
	1630 S				1625	CO s (75), CN s (23), C$^\alpha$CN d (11)
				1486		CN s (33), C$^\alpha$C s (26), CO ib (17), ND ib (17), NC$^\alpha$ s (16)
					1474	CN s (29), C$^\alpha$C s (29), CO ib (18), NC$^\alpha$ s (16), ND ib (15)
	1460 S		1464			CN s (37), C$^\alpha$C s (27), CO ib (21)
		1463				CN s (36), C$^\alpha$C s (28), CO ib (20)
			1244			NC$^\alpha$ s (47), CD$_2$ w (34), C$^\alpha$C s (23), ND ib (15)
		1243				NC$^\alpha$ s (47), CD$_2$ w (35), C$^\alpha$C s (23), ND ib (15)
				1107		CD$_2$ w (37), CD$_2$ b (27), C$^\alpha$C s (19)
	1101 W				1106	CD$_2$ w (37), CD$_2$ b (28), C$^\alpha$C s (17)
		1099				CD$_2$ b (37), NC$^\alpha$ s (32)
	1075 W		1098			CD$_2$ b (37), NC$^\alpha$ s (32)
				1056		ND ib (50), CD$_2$ b (24)
					1046	CD$_2$ b (56), CD$_2$ w (34)
				1040		CD$_2$ b (35), CD$_2$ w (30), ND ib (17)
					1026	ND ib (61), CO ib (14)
		1025				CD$_2$ b (54)
	1016 W		1024			CD$_2$ b (54)
					978	NC$^\alpha$ s (66), CN s (11)
				977		NC$^\alpha$ s (66), CN s (11)
		926				ND ib (40), CD$_2$ w (26), CD$_2$ tw (23)
	950 W		925			ND ib (37), CD$_2$ w (28), CD$_2$ tw (26)
				923		CD$_2$ tw (60)
	923 W				922	CD$_2$ tw (60)
		896				CD$_2$ tw (66), ND ib (18)
	901 W		895			CD$_2$ tw (63), ND ib (19)
		878				CD$_2$ w (20), CD$_2$ r (17)
	866 W		875			CD$_2$ r (18), CD$_2$ w (17)
					873	CN s (24), CD$_2$ tw (16)
				870		CN s (26), CD$_2$ tw (16)
		827				CD$_2$ r (30), CO ob (18), CD$_2$ w (14)

Table III (*Continued*)

observed[a]		calculated				
Raman	IR	A$_g$	A$_u$	B$_g$	B$_u$	potential energy distribution[b]
			826			CD$_2$ r (29), CO ob (17), CD$_2$ w (14)
				795		CD$_2$ r (55), C$^\alpha$C s (13)
					792	CD$_2$ r (56), C$^\alpha$C s (13)
					687	C$^\alpha$C s (18), CO ib (14), NC$^\alpha$C d (13), CD$_2$ r (12)
				686		C$^\alpha$C s (17), CO ib (15), NC$^\alpha$C d (14), CD$_2$ r (13)
				623		CO ob (62), CN t (17)
	605 M				613	CO ob (69), CN t (11)
		591				CO ib (54), C$^\alpha$C s (17), ND ib (11)
			591			CO ib (54), C$^\alpha$C s (16), ND ib (11)
	554 M		542			CN t (35), CO ob (35), CD$_2$ r (14)
					532	C$^\alpha$CN d (47), CD$_2$ w (14)
				532		C$^\alpha$CN d (48), CD$_2$ w (11), CN t (10)
		531				CO ob (50), CD$_2$ r (29)
				512		CN t (56), ND ob (42), ND···O ib (21), CO ob (17), D···O s (13), CD$_2$ w (12)
	493 S		509			CN t (41), ND ob (30), CO ob (17), ND···O ib (16), CO ob (15), D···O s (12)
	493 S				509	CN t (70), ND ob (39), ND···O ib (24), D···O s (14)
		502				CN t (80), ND ob (32), ND···O ib (26), D···O s (15)
				294		CO ib (32), NC$^\alpha$C d (26)
					293	CO ib (34), NC$^\alpha$C d (26)
		272				C$^\alpha$CN d (51), NC$^\alpha$C d (23)
			272			C$^\alpha$CN d (54), NC$^\alpha$C d (20)
					225	CNC$^\alpha$ d (35), ND ob (18), CO ib (11)
				225		CNC$^\alpha$ d (36), ND ob (26), CO ib (14)
			214			CNC$^\alpha$ d (68), CO ib (11)
		203				CNC$^\alpha$ d (75)
			176			ND ob (69), CO ob (20), CD$_2$ w (11)
		174				ND ob (66), CO ob (16), CD$_2$ w (13), C$^\alpha$CN d (13)
					139	D···O s (48), CN t (44), ND ob (34), C$^\alpha$C t (11)
		133				D···O s (31), CN t (29), NC$^\alpha$C d (11)
				109		D···O s (78), CN t (18)
			100			NC$^\alpha$C d (43), C$^\alpha$C t (17), ND ob (15), NC$^\alpha$ t (15)
		80				ND ob (43), NC$^\alpha$C d (27), CN t (23), D$^\alpha$···D$^\alpha$ s (14), NC$^\alpha$ t (14)
				69		C$^\alpha$C t (35), NC$^\alpha$ t (25), CN t (21), ND ob (20), ND···O ib (17)
			35			ND···O ib (38), CO···D ib (28), ND ob (19), D···O s (16)
				31		ND···O ib (36), CO···D ib (31), CN t (27), ND ob (16), NC$^\alpha$ t (12)
		12				ND t (52), CO t (34)
						-(^{15}NHCH$_2$CO)-$_n$
		3263				NH s (98)
			3263			NH s (98)
				3263		NH s (98)
	3262 S[c]				3263	NH s (98)
				2935		CH$_2$ as (98)
		2934				CH$_2$ as (98)
	(2929 W)[d]				2929	CH$_2$ as (99)
	(2929 W)		2928			CH$_2$ as (99)
				2866		CH$_2$ ss (98)
		2865				CH$_2$ ss (98)
	(2869 VW)		2861			CH$_2$ ss (99)
	(2869 VW)				2861	CH$_2$ ss (99)
				1694		CO s (77), CN s (14), C$^\alpha$CN d (11)
	1685 M		1687			CO s (76), CN s (18), C$^\alpha$CN d (11)
		1675				CO s (76), CN s (19), C$^\alpha$CN d (11)
	1635 S				1640	CO s (71), CN s (20), C$^\alpha$CN d (11)
				1592		NH ib (56), CN s (18), C$^\alpha$C s (12)
					1563	NH ib (50), C$^\alpha$C s (17), CN s (15)
	1503 S		1503			NH ib (32), CN s (27), C$^\alpha$C s (19), CO ib (15)
		1502				NH ib (32), CN s (26), C$^\alpha$C s (20), CO ib (15)
		1452				CH$_2$ b (67), CH$_2$ w (14), NH ib (13)
			1452			CH$_2$ b (66), CH$_2$ w (14), NH ib (13)
				1441		CH$_2$ b (96)
	1431 S				1438	CH$_2$ b (96)
		1414				CH$_2$ w (42), CH$_2$ b (30), NH ib (15)
	(1408 W)		1414			CH$_2$ w (41), CH$_2$ b (33), NH ib (15)
				1336		CH$_2$ w (83), NH ib (11)
	(1338 W)				1332	CH$_2$ w (80)
				1301		NH ib (26), CO ib (19), CN s (19), C$^\alpha$C s (15)
	(1295 W)				1285	NH ib (37), C$^\alpha$C s (18), CO ib (17), CN s (13)
		1252				CH$_2$ tw (77), CH$_2$ w (17)
			1252			CH$_2$ tw (77), CH$_2$ w (17)
				1242		CH$_2$ tw (92)
	1235 M				1240	CH$_2$ tw (92)
		1208				NH ib (24), NC$^\alpha$ s (23), CH$_2$ w (20), CH$_2$ tw (16), CN s (15)

Table III (*Continued*)

observed[a]		calculated				
Raman	IR	A_g	A_u	B_g	B_u	potential energy distribution[b]
	1210 W		1207			NH ib (24), NC$^{\alpha}$ s (23), CH$_2$ w (20), CH$_2$ tw (16), CN s (15)
		1141				NC$^{\alpha}$ s (58), C$^{\alpha}$C s (12), NH ib (10)
			1141			NC$^{\alpha}$ s (58), C$^{\alpha}$C s (12), NH ib (10)
				1005		NC$^{\alpha}$ s (79), C$^{\alpha}$C s (10)
	1010 M				1004	NC$^{\alpha}$ s (79), C$^{\alpha}$C s (10)
		997				CH$_2$ r (49), CO s (10)
			995			CH$_2$ r (52)
	(987 W)				974	CH$_2$ r (72)
				973		CH$_2$ r (74)
		939				CH$_2$ r (25), CN s (13), C$^{\alpha}$C s (13), NC$^{\alpha}$C d (10)
	(936 M)		933			CH$_2$ r (22), CN s (14), C$^{\alpha}$C s (14), NC$^{\alpha}$C d (11), CO s (10)
	(888 W)				881	C$^{\alpha}$C s (30), CN s (24), CO s (14)
				881		C$^{\alpha}$C s (32), CN s (27), CO s (13)
				765		CO ib (16), CN t (16), NC$^{\alpha}$ s (14), C$^{\alpha}$C s (13), NC$^{\alpha}$C d (11), CNC$^{\alpha}$ d (10), NH ob (10)
					764	CO ib (17), C$^{\alpha}$C s (17), NC$^{\alpha}$ s (15), NC$^{\alpha}$C d (12), CNC$^{\alpha}$ d (11)
				735		CN t (60), NH···O ib (14), H···O s (10), NH ob (10)
			718			CN t (79), NH ob (26), NH···O ib (23), H···O s (11)
	(708 S)				717	CN t (73), NH···O ib (18), NH ob (15), H···O s (10)
		702				CN t (79), NH ob (29), NH···O ib (25), H···O s (15)
		625				CO ib (34), CO ob (26)
	626 W		624			CO ib (35), CO ob (25)
	611 M				618	CO ob (69), NH ob (14), C$^{\alpha}$CN d (12), NC$^{\alpha}$C d (10)
				609		CO ob (63), NH ob (18), C$^{\alpha}$CN d (16), NC$^{\alpha}$C d (10)
					581	C$^{\alpha}$CN d (49), CO ob (15)
				579		C$^{\alpha}$CN d (46), CO ob (20), CH$_2$ w (10)
		578				CO ob (44), CO ib (30), C$^{\alpha}$C s (12)
	(589 M)		577			CO ob (44), CO ib (29), C$^{\alpha}$C s (11), CH$_2$ r (10)
				321		NC$^{\alpha}$C d (21), CO ib (17), NH ob (15)
	(320 W)				318	NC$^{\alpha}$C d (22), CO ib (18), NH ob (15)
		290				C$^{\alpha}$CN d (51), NC$^{\alpha}$C d (21), NC$^{\alpha}$ s (11)
	(285 W)		290			C$^{\alpha}$CN d (55), NC$^{\alpha}$C d (19), NC$^{\alpha}$ s (12)
					252	CNC$^{\alpha}$ d (41), CO ib (28)
				249		CNC$^{\alpha}$ d (41), CO ib (30), NH ob (15)
	(217 W)		224			CNC$^{\alpha}$ d (68), H···O s (10), CO ib (10)
		212				CNC$^{\alpha}$ d (75)
			176			NH ob (70), CO ob (19), CH$_2$ w (11)
		174				NH ob (67), CO ob (15), CH$_2$ w (12), C$^{\alpha}$CN d (11), NC$^{\alpha}$ s (10)
	(140 M, br)				139	H···O s (46), CN t (45), NH ob (37), C$^{\alpha}$C t (12)
		135				H···O s (29), CN t (25), NC$^{\alpha}$C d (15)
				110		H···O s (78), CN t (18)
			108			NC$^{\alpha}$C d (46), NH ob (16), C$^{\alpha}$C t (16), NC$^{\alpha}$ t (14)
		87				NH ob (43), CN t (27), NC$^{\alpha}$C d (26), H$^{\alpha}$···H$^{\alpha}$ s (13), NC$^{\alpha}$ t (12), H···O s (10)
				70		C$^{\alpha}$C t (35), NC$^{\alpha}$ t (24), NH ob (22), CN t (22), NH···O ib (16)
			37			NH···O ib (38), CO···H ib (28), NH ob (18), H···O s (17)
				31		NH···O ib (36), CO···H ib (31), CN t (22), NH ob (17), NC$^{\alpha}$ t (13)
		12				NH t (52), CO t (34)

[a] S = strong, M = medium, W = weak, V = very, br = broad. [b] s = stretch, as = antisymmetric stretch, ss = symmetric stretch, b = angle bend, ib = in-plane angle bend, ob = out-of-plane angle bend, w = wag, r = rock, t = torsion, d = deformation, tw = twist. Only contributions of 10% or greater are included. [c] Unperturbed frequency (cf. ref 5; same approach used for other isotopic species). [d] From $-(NHCH_2CO)-_n$, presumed to be unshifted (ref 17).

diagonal force constant is that of $f(CNC^{\alpha})$ (from 0.787 to 0.687), and this is undoubtedly due primarily to the introduction of the new off-diagonal constant $f(CNC^{\alpha},C^{\alpha}NH)$. The relatively large changes in some of the off-diagonal force constants are probably mainly a result of the additional constants in the force field. Dispersions in the refined force constants (average percent in parentheses) were $f = 0.08–0.17$ (14), $f = 0.01–0.08$ (30), and $f \leq 0.01$ (53).

Results and Discussion

The observed and calculated frequencies of APRS (Gly I)$_n$ and its isotopic derivatives are given in Table III. The infrared data for the deuterated species are from Suzuki et al.[17] For the ^{15}N molecule no spectra were shown,[17] and only the shifts for some bands were tabulated. These are listed in Table III, with (presumed) unshifted bands given in parentheses.

The assignment of the modes for $-(NHCH_2CO)-_n$ is the same as that given previously.[5] The average discrepancy between observed and calculated frequencies is somewhat better for our present calculation (5.4 vs. 6.2 cm^{-1} for frequencies below 1700 cm^{-1}), but there is a significant improvement with respect to the prediction of CH$_2$ wag and CH$_2$ twist modes, in particular the observed bands at 1410, 1408, 1338, and 1234 cm^{-1}. There is also some improvement in the low-frequency region for CNC$^{\alpha}$ deformation modes. Many modes in the two calculations have somewhat different potential energy distributions, which is not surprising since different force constants as well as different values for some of the same force constants were used. In most cases the same internal coordinates contribute, though to somewhat differing extents. In some instances there is a significant difference in the contributing coordinates. For example: 1460 (Raman)—CH$_2$ bend (97)[5] vs. CH$_2$ bend (66), CH$_2$ wag (16); 1410 (Raman), 1408 (infrared)—CH_2 wag (60), NH ib (19), $C^{\alpha}C$ s (17)[5] vs. CH_2 wag (40), CH_2 bend (33), NH ib (13); 1234 (Raman)—CH_2 twist (76), NH ib (12)[5] vs. CH_2 twist (93). A similar situation exists for the mode at 82 cm^{-1}, due primarily to the change in the value of $f(H^{\alpha}\cdots H^{\alpha})$.

For the deuterated molecules the overall agreement is reasonable and comparable to that obtained by Abe and Krimm.[4] It must be remembered that in the present study the frequencies of the isotopic molecules were not included in the least-squares refinement, which was done in the earlier work[4] (the latter also used the APPS structure). It should not be surprising, therefore, if, for example, CD_2 stretching frequencies are poorly reproduced, since they contain anharmonicities significantly different from those of CH_2 modes. In fact, it was for this reason that isotopic frequencies were not included in the present refinement, since we did not wish to bias the typical calculations on hydrogenated molecules. For $-(NDCH_2CO)-_n$ the average discrepancy for the observed infrared bands below 1700 cm^{-1} is 5.5 cm^{-1}, comparable to what we found for $-(NHCH_2CO)-_n$. We have determined the unperturbed ND stretching frequency by the same Fermi resonance analysis as used previously[5] (although in this case relative intensities could only be roughly estimated from the given data[17]). The disagreement with the calculated value is probably due to anharmonicity effects. (The combination band here is also of lower frequency, $\sim$2425 cm^{-1}, than the fundamental and probably involves modes with CN stretch and ND in-plane bend; e.g., 1475 (A_u) + 939 (B_g) = 2414 (B_u) and 1486 (B_g) + 950 (A_u) = 2436 (B_u).) The downward shift of about 5 cm^{-1} in the amide I modes is well reproduced. The so-called amide II′ mode, at 1475 cm^{-1}, is seen to contain a large $C^{\alpha}C$ stretch contribution in addition to the expected[17] CN stretch contribution, as found before.[4] The so-called amide III′ mode, at 950 cm^{-1}, thought to be mainly ND in-plane bend,[17] is, in fact, largely CH_2 rock, as noted earlier.[4] And as with $-(NHCH_2CO)-_n$, CO in-plane bend and CO out-of-plane bend mix heavily in the so-called amide VI mode. For $-(NHCD_2CO)-_n$ the large drop in amide II, from 1517 to 1498 cm^{-1}, is reproduced only qualitatively. This may be due to the fact that different transition dipole coupling parameters are to be associated with the deuterated as compared to the fully hydrogenated molecule (the potential energy distributions are certainly different). The CD_2 bend, wag, and twist frequencies are well reproduced, except for the wag plus rock mode at 866 cm^{-1}. The presence of the wag contribution may also account for the discrepancy in the 564-cm^{-1} band. For $-(NDCD_2CO)-_n$ bands at 1075 and 950 cm^{-1} show large discrepancies, but the other bands are well reproduced. Considering that the force field was transferred from the hydrogenated molecule without change and that anharmonicities are not taken into account, the present force field can be considered to reproduce the 39 frequencies (below 1700 cm^{-1}) of the deuterated molecules quite well.

The shifts predicted for $-(^{15}NHCH_2CO)-_n$ are seen to be in good agreement with those observed. The observed 14-cm^{-1} shift in amide II in particular is well reproduced, as is the next largest shift in the skeletal mode at 1016 cm^{-1}. It is also of interest that the 10-cm^{-1} decrease in the unperturbed NH stretch is well reproduced by the calculation.

Conclusions

The present study has resulted in a small modification of the previously refined[5] force field for (Gly I)$_n$. This has produced, however, significant improvement in the prediction of most of the CH_2 modes, with about the same agreement for the others. This force field satisfactorily accounts for the frequencies of isotopically substituted molecules and, as we will see in the next paper, is better transferable to β-(Ala)$_n$. It thus provides a more secure basis for the vibrational analysis of peptide systems.

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