Theoretical Prediction of Vibrational Spectrum of *N*-Glycylglycine Hydrochloride: An ab Initio Study

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A complete set of force constants and their corresponding scale factors were obtained by fitting the experimental vibrational frequencies of seven isotopomers of glycine hydrochloride (GH) to the ab initio force field obtained at the HF/6-31G** level for the lowest energy conformation. A recently developed fitting procedure is used for this purpose. The fitting is extremely successful in producing a force field which reproduces the frequencies within an average deviation of 9.7 cm^{-1} from the experimentally observed fundamentals for all of the seven isotopomers. A conformational study was undertaken for glycylglycine hydrochloride (GGH) at the same level of theory. The scale factors of GH were used to obtain the scaled ab initio force field of the minimum energy conformer of GGH, which in turn was used to predict the vibrational frequencies and their potential energy distribution (PED). The excellent agreement between the experimental and predicted fundamentals offers a "real" example to the concept of building a reliable force field from a smaller unit to a larger unit, i.e., of a dipeptide from its parent amino acid.

Introduction

Due to the recent advances in quantum chemical methodology, an accurate description of molecular force field is possible for small molecules by extending the atomic orbital basis sets and including the electron correlation. Such a physical representation of a typical macromolecular system of interest in structural biology is not possible due to limited computational resources. As a result, the simulation of proteins and nucleic acids and their interactions have led to a large number of empirical force fields.[1−6] For a better description of molecular dynamics and molecular mechanics of these large systems, an accurate knowledge of force field parameters are essential. A new approach has been introduced in this regard by using the ab initio Hatree−Fock calculations, employing an optimal basis set to derive a preliminary quantum mechanical force field, whose parameters are then systematically scaled by fitting to the available experimental data.[7] These scale factors are then transferred to structurally related larger systems. This scaled quantum mechanical (SQM) approach proved very successful for a large number of organic molecules.[8,9] However, the success is very limited when the SQM procedure is applied to amino acids. Since there is no symmetry in the amino acids (point group C_1), each force constant is different from the other; many sets of scale factors give an equally good fit, and hence, it becomes difficult to obtain a unique solution.[10] A second, equally difficult problem is that the ab initio potential energy distribution (PED) is different from the experimentally obtained PED, implying that the ab initio result is a poor model for amino acids.[11] This is because the ab initio calculation refers to the isolated molecule in the gas phase. In this phase, it is not in the zwitterion state[12] and it may exhibit intramolecular H-bonding, which is absent in solution or the solid state.[11,13] Attempts are being made to improve the model explicitly by including water molecules in the calculation (supermolecular calculation) or implicitly by introducing a dielectric medium (Onsager reaction field).[10,14,15] A SQM force field calculation on the glycine cation supermolecule is available for cis and trans conformations at HF/4-31G* level.[10] Such supermolecular calculations, although aimed at building generalized scale factors for peptides, are difficult to extend to higher systems because of the increase in the number of atoms included as water molecules. Also the water modes get mixed up with the normal modes, and the discussion in terms of single molecule force constants becomes difficult. Alanine zwitterion is studied by the reaction field approach in a water environment.[15] This improves the ab initio model, although the agreement is not very good with the experimental PED.

An attractive solution to this problem could be the transfer of scale factors from smaller amino acids to the larger dipeptides for which the ab initio model correctly describes the gross features of experimental vibrational spectra. Ab initio calculations of isolated amino acids in their cationic or anionic forms (in acidic or basic solution) grossly resemble the experimental features because the intramolecular H-bonding is less pronounced in these molecules compared to their zwitterions. Because we are trying to describe the molecular features in condensed phase where intramolecular H-bonding does not exist, the basis set has to be chosen in such a way that helps to describe the features of such intramolecular H-bonding to a negligible or very small extent. Although this would represent a less satisfactory prediction for the isolated molecule, it has the merit of mimicking the actual situation in solution or solid phases. Hence, the present study involves a complete conformational and vibrational analysis of GH and GGH and transfer of scale factors between them to obtain a reliable theoretical force field for the smallest dipeptide hydrochloride.

Many conformational and vibrational analyses of neutral amino acids are found in the literature.[16,17] A complete vibrational analysis of amino acids in the zwitterionic or any other ionic form is mainly limited to glycine,[10,12,14] alanine,[11] cysteine, and serine.[13] To the best of our knowledge, a complete ab initio vibrational analysis of any peptide is limited to our earlier study of GGH.[18] An experimental Raman study of glycylglycine zwitterion (GG) and its normal mode analysis was reported by Lagant et al.[19]

Methodology

Calculations for both GH and GGH were performed with the Gaussian 90 and 94 programs.[20] The geometry optimizations

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and frequency calculations were done using 4-21G and 6-31G** basis sets. The ab initio force constants and frequencies of GH were calculated analytically and that of GGH numerically. The Cartesian force constant matrix was transformed to the nonredundant local coordinate space following the recommendation of Pulay et al.[21] The fitting procedure described in detail in our earlier papers was used to get the scale factors for GH by fitting the frequencies of seven different isotopomers simultaneously.[22] A flow chart of the fitting algorithm is available as Supporting Information. The fitting is extremely successful in producing an average deviation of 9.7 cm^{-1} from the available experimental data. The ab initio force constants of GGH are scaled using the scale factors of GH. Durig's scaling procedure[23] was applied when there is no equivalent local symmetry coordinates between the two compounds. Durig's scaling involves the scale factor 0.9 for stretching, 0.8 for bending, and the geometric mean for the off-diagonal elements. The experimental IR spectra of GGH was taken from our earlier reported spectra.[18] Glycylglycine methyl ester hydrochloride (GGMH) was prepared by reacting $SOCl_2$ with *N*-glycylglycine in methanol. The solution was dried under high vacuum. The IR spectrum was recorded using a Perkin-Elmer spectrophotometer.

Results

Amino acid hydrochlorides in solution dissociate into an amino acid cation and Cl^-, and, hence, to a good approximation, the spectral features could be accounted for by the cation. Similar treatments gave successful results for other systems, for example, acetylcholine.[24] In solid state, each Cl^- is ionically bonded to the planar H-atom of the N^+H_3 group with a bond distance of 2.59 Å in GH. The room temperature spectra of NH_4Cl and NH_4Br are essentially identical, indicating that the anion has very small effect on the spectra.[25] The differences between the solid and solution phase spectra could be accounted for in most cases by the phase change (mainly the strong intermolecular H-bonded network in the crystal structure vs intermolecular H-bonding in a dielectric medium). Thus, as a reasonable approximation, the cations can be considered as a good theoretical model for the vibrational spectra of amino acid hydrochlorides, and, hence, in the present study optimization and frequency calculations were performed with the respective cations of GH and GGH. Similar observations have been made on $C_5H_5^-Li^+$, $C_5H_5^-Na^+$, and $C_5H_5^-K^+$.[26] Furthermore, the fully optimized structure of GH at the HF/6-31G** level of calculation by including Cl^- explicitly results in the dissociation of GH into neutral amino acid and HCl.

It is known that the electron correlation may contribute significantly to those frequencies which comprise vibrations of double bonds. To see the effect of correlation, a separate calculation has been performed on CH_3COOH at the HF/6-31G** and MP2/6-31G** levels of calculation. Since the C═O bond is very well-characterized as a localized mode in related systems, the final results will still be a good approximation to the correct force constants and frequencies. Our calculated results on acetic acid at both levels are very similar after scaling, indicating that part of the correlation is included during fitting using experimentally observed frequencies (see Tables SIX and SX in the Supporting Information). [In acetic acid, $f_{C=O}$ is 16.358/12.613 (in HF/6-31G**) and 13.373/12.257 (in MP2/6-31G**) (unscaled/scaled)].

Conformations of GH. The conformational space of GH has been studied by several authors using ab initio theory. These studies clearly indicate that the lowest energy conformation is basis set dependent.[27,28] Since we are looking for a conformation in which the intramolecular H-bonding will be a minimum so that it will mimic the solution or solid state spectra, we used 4-21G, a low-level basis set, and 6-31G**, a high-level basis set. For the present work we took only the two lowest energy conformations of GH from the earlier study.[27] At the 4-21G level C1 is the lowest energy form, whereas, at 6-31G**, C2 is the most stable one (Figure 1). Inclusion of the correlation at the MP2 level does not improve 4-21G results, while C2 changes to a structure closer to C1 at the 6-31G** level, indicating that the HF/4-21G calculation reproduces the structure close to the global minima, though C2 is closer to the crystal structure.[28] In all the cases the frequency calculations on the optimized structure were done to make sure that they are real minima. Since the minimum energy conformation at HF/6-31G** does not have the intramolecular H-bonding and also replicates the crystal structure, this basis set is used for the vibrational spectral study.

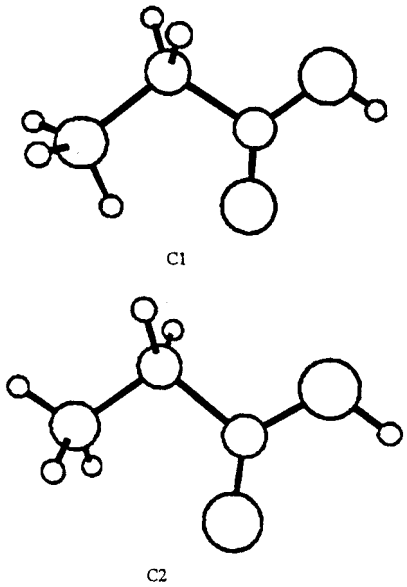

Figure 1. HF/6-31G** optimized structures of the two conformers of GH.

TABLE 1: Relative Energies (kJ/mol) of GH and GGH[a]

structure	HF/6-31G**	MP2/6-31G**
	GH	
C1	15.30 (0.00)	0.03
C2	0.00 (5.07)	0.00
	GGH	
C1	0.0	0.0
C2	2.2	7.1
C3	21.2	18.5
C4	23.3	25.4
C5	36.2	33.5
C6	38.2	40.2
C7	61.6	54.8
C8	60.7	53.9

[a] The numbers in the parentheses are the 4-21G energies.

Conformations of GGH. Eight possible different conformations were selected by rotating the N-terminal and C-terminal groups of GGH. Each conformation is fully optimized at the 6-31G** basis set. The optimized structures are given in Figure 2, and the final results of different calculations are listed in Table 1. C1 is the minimum energy structure. Further MP2/6-31G** single point calculations were performed to see the effect of correlation on the relative energies of these eight conformations. Frequency calculation was done only on the minimum energy conformation.

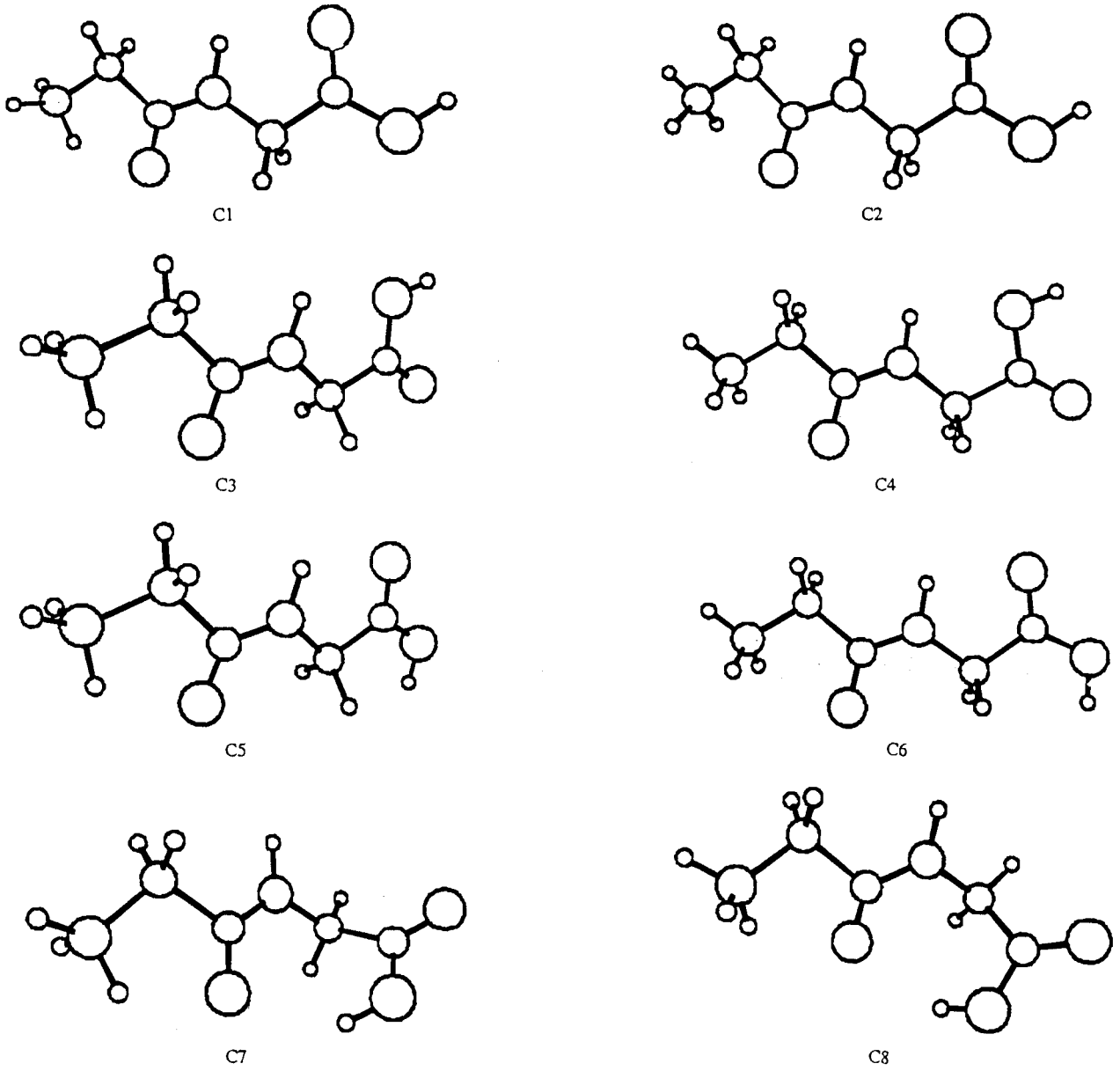

Figure 2. HF/6-31G** optimized structures of the eight conformers of GGH.

Vibrational Frequencies of GH. The solution phase IR and Raman spectra of several isotopomers of GH were reported by Williams et al.[10] However, the supermolecular calculation with water molecules introduces strong coupling between the vibrational modes of GH and water. As a result regions below 600 cm^{-1} are not very well described in their work. Also since the least squares method has not lead to unique assignment, they constrained the scale factors in their SQM approach to yield PEDs that were in agreement with their empirical assignment. In the present work the fitting of the experimental frequencies of seven isotopomers produced a better fit than that of Williams et al. except for the peak at 568 cm^{-1} in GH-d_0. For this mode the absolute deviation from the fitted one is 30 cm^{-1}. It is possible that this frequency might have been misassigned. For all fundamentals the assignments are very close to those of unscaled ab initio normal modes. The PEDs of the scaled force field are in good agreement with that of Williams et al.,[10] and, hence, the assignment for GH will not be discussed further. The force field cannot be compared, as our results are based on an isolated molecule. The fitted frequencies and their PEDs for GH-d_0 are given in Table 2, and the corresponding fitted frequencies for the isotopomers are given in Table 3.

Vibrational Frequencies of GGH. The frequencies obtained from the scaled force field and the corresponding PEDs of GGH are shown in Table 4. The predicted frequencies are in excellent agreement with the available experimental data with an average deviation of 7.6 cm^{-1}. For a comparative study, the experimental frequencies of GG and GGMH are also given in the table.

The ν(C═O) acid and ν(C═O) amide bands are predicted at 1738 and 1676 cm^{-1} and are observed at 1746 and 1677 cm^{-1}. This is in agreement with the 1724 and 1678 cm^{-1} bands of the corresponding GGMH. The C═O is observed at 1682 cm^{-1} in GG.[19]

Both of the $\delta_a(N^+H_3)$ modes are predicted at 1641 and 1602 cm^{-1} and are not observed in our IR spectra. However, the 1629 and 1611 cm^{-1} Raman bands of GG[19] are in very good agreement with our predicted numbers. These modes appear as degenerate bands at 1607 cm^{-1} in GH in accordance with the prediction. The 1648 cm^{-1} band and the weak shoulder at 1622 cm^{-1} in the corresponding GGMH spectra compare well with these assignments. The asymmetric NH(amide) bend is predicted at 1593 cm^{-1} along with ν(CN), ν(C═O) (amide), and ν(NC′) is assigned to 1584 cm^{-1}. This amide II mode is

TABLE 2: Fitted Vibrational Frequencies of GH (cm^{-1})

sym species	6-31G** (scaled)	assignments	expt[a]	SQM
1	3412	ν(OH)	(3200)	
2	3179	$\nu(N^+H)$	3182	
3	3124	$\nu(N^+H)$	3152	
4	3060	$\nu(N^+H)$	3058	
5	3019	ν(CH)	3012	3022
6	2961	ν(CH)	2973	2961
7	1746	ν(C═O)	1740	1750
8	1616	$\delta_a(N^+H_3)$	1607	1618
9	1610	$\delta_a(N^+H_3)$	1607	1594
10	1512	$\delta_s(N^+H_3) + \omega(CH_2)$	1512	1518
11	1489	$\delta_s(N^+H_3) + \omega(CH_2) + \nu$(CO)	(1484)	1476
12	1427	$\nu(CH_2)$	1435	1434
13	1378	ν(COH) + $\omega(CH_2)$ + ν(CO)	1378	1384
14	1328	$t(CH_2) + \rho(N^+H_3)$	1320	1324
15	1252	ν(CO) + δ(COH)	1263	1284
16	1148	$\rho(N^+H_3) + \omega(CH_2) + \nu(CN^+)$	1135	1153
17	1121	$t(CH_2) + \rho(N^+H_3)$	1125	1137
18	1042	$\nu(CN^+)$	1044	1058
19	923	$\rho(CH_2) + \rho(N^+H_3) + \gamma$(CO)	917	923
20	884	ν(CC) + $\rho(N^+H_3)$	873	880
21	657	τ(CO) + γ(CO)	657	669
22	598	δ_a(CO) + $\delta(N^+CC)$	568	563
23	521	γ(CO) + τ(CO) + $\rho(CH_2)$	504	453
24	498	δ_s(CO)	(483)	
25	297	$\delta(N^+CC) + \delta_s$(CO) + δ_a(CO)	301	250
26	174	$\tau(CN^+) + \tau$(CC)	(175)	
27	34	τ(CC) + $\tau(CN^+)$	(35)	

[a] Experimental frequencies are taken from ref 10. Since the fitting algorithm requires all of the experimental frequencies at least for one isotopic species, the numbers in parentheses are introduced as a good guess for GH-d_0 and do not have any other significance.

observed at a lower frequency (1531 cm^{-1}) in the zwitterion. The 1535 cm^{-1} band observed in the GGMH spectrum is in agreement with this assignment. The symmetric N^+H_3 deformation predicted at 1472 cm^{-1} agrees very well with the 1480 cm^{-1} in the zwitterionic spectra. This mode is assigned to the 1452 cm^{-1} peak in the corresponding GGMH. Both of the $\rho(N^+H_3)$ modes are predicted at 1155 and 1126 cm^{-1} and are observed at 1135 and 1117 cm^{-1} in the GGH spectra, 1158 and 1100 cm^{-1} in the zwitterion, and 1130 and 1090 cm^{-1} in the GGMH. In many amino acids these $\rho(N^+H_3)$ modes appear as two closely spaced bands around 1100−1150 cm^{-1}.[29,30]

The observed band at 1487 cm^{-1} is predicted very well at 1486 cm^{-1} and is assigned to the mixed mode of $\omega(C'H_2)$, $\nu(C'C)$, ν(CO), and $\omega(CH_2)$. The various CH_2 bending modes ($\delta(CH_2)$, $\omega(CH_2)$ and $t(CH_2)$) are predicted at 1443, 1433, 1408, 1329, and 1242 cm^{-1} and are assigned to the observed bands at 1434, 1434, 1410, 1308, and 1219 cm^{-1}, respectively. The 1447 cm^{-1} Raman band assigned to $\delta(CH_2)$ by Lagant et al. in the zwitterion spectra agrees very well with our predicted 1443 cm^{-1} band. This mode is assigned to the observed band at 1437 cm^{-1} in the GGMH. The $\omega(CH_2)$ mode at 1408 cm^{-1} is assigned to 1399 and 1402 cm^{-1} in the corresponding GG and GGMH. The CH_2 rocking modes are predicted at 1002 and 925 cm^{-1}. The higher one is assigned to the observed band at 1013 cm^{-1} and is consistent with the earlier assignment of Lagant et al. at 1007 cm^{-1} in the zwitterionic spectra for this mode. Although there is no band corresponding to the lower one in our hydrochloride spectra, this agrees well with the 918 cm^{-1} band assignment of the zwitterionic spectra.[19]

The predicted band at 1362 cm^{-1} is assigned to δ(COH), and $\omega(C'H_2)$ is in agreement with the observed band at 1350 cm^{-1}. This band is observed at 1378 cm^{-1} in GH and is consistent with this assignment. There is no corresponding mode in the zwitterion spectra, but it appears at 1362 cm^{-1} in the spectrum of GGMH. The $\nu(N^+C)$ and one of the $\nu(CC') + \nu$(CC) modes predicted at 1050 and 907 cm^{-1} are in excellent agreement with the observed bands of all three compounds and also consistent with the 1044 and 873 cm^{-1} bands of GH.

Bands predicted at 700 and 661 cm^{-1} agree very well with the observed bands at 708 and 661 cm^{-1} in the hydrochloride spectra, 708 and 665 cm^{-1} in the zwitterion, and 708 and 644 cm^{-1} in the GGMH. Bands below 600 cm^{-1} are not available for GGH, and, hence, the predicted numbers below 600 cm^{-1} are compared with the zwitterionic spectra of Lagant et al.[19]

TABLE 3: Fitted Vibrational Frequencies of All Seven Isotopomers of GH (cm^{-1})

$N^+H_3CH_2COOH$		$N^+H_3{}^{13}CH_2COOH$		$N^+H_3CH_2{}^{13}COOH$		$N^+H_3CD_2COOH$		$N^+D_3{}^{13}CH_2COOD$		$N^+D_3{}^{13}CH_2COOD$		$N^+D_3CH_2{}^{13}COOD$	
expt	calc	expt	calc	expt	calc	expt	calc	expt	calc	expt	calc	expt	calc
	3412		3412		3412		3412		2484		2484		2484
3182	3179		3179		3179	3182	3179	2341	2347		2347		2347
3152	3124		3124		3124	3152	3124	2263	2306		2306		2306
3058	3060		3060		3060	3058	3060	2203	2199		2199		2199
3012	3019		3007		3019	2232	2249	3015	3019		3007		3019
2973	2961		2955		2961	2166	2161	2975	2961		2955		2961
1740	1746	1741	1745	1700	1703	1741	1744	1733	1732	1732	1731	1688	1687
1607	1616	1608	1616	1614	1614	1608	1614		1160	1166	1159	1168	1160
1607	1610	1608	1609	1614	1610	1608	1607		1153		1152		1153
1512	1512	1510	1507	1520	1507	1518	1503		1186	1166	1182	1168	1186
	1489		1481		1475	1443	1455		1480	1435	1464	1438	1464
1435	1427	1431	1424	1437	1427	1044	1037	1429	1427	1411	1423	1406	1427
1378	1378	1360	1374	1370	1367	1317	1302	1340	1313	1336	1311	1321	1290
1320	1328	1316	1325	1320	1328	1201	1217	1278	1272	1277	1270	1271	1271
1263	1252	1263	1252	1246	1243	1210	1227	1073	1078	1060	1076	1066	1078
1135	1148	1133	1140	1139	1147	926	921	780	768	775	764	776	766
1125	1121	1113	1118	1119	1117	918	917	815	793	805	793	808	789
1044	1042	1027	1024	1044	1042	1112	1109	1008	1003	989	986	1007	1003
917	923	915	919	910	916	804	802	1043	1042	1032	1032	1025	1034
873	884	864	873	869	881	842	837	951	956	941	945	949	956
657	657	648	657	656	653	644	632	618	598	608	597	614	589
568	598	566	595	559	596		592	561	552	558	550	555	550
504	521	501	521	502	514		463		419		419		417
	498		496		497	480	487	485	470	483	468	483	468
301	297	301	296	301	296	301	295	287	275	290	275	287	274
	174		172		174		166		148		146		148
	34		34		34		33		27		27		27

TABLE 4: Predicted Vibrational Frequencies of GGH (cm^{-1})

sym species	6-31G** (scaled)	assignments	GGH expt	GG expt[a]	GGMH expt
1	3436	ν(OH)			
2	3265	ν(NH)		3285	
3	3161	$\nu(N^+H)$			
4	3109	$\nu(N^+H)$			3080
5	3017	ν(CH)		3013	
6	2977	ν(C′H)		2960	2960
7	2964	$\nu(N^+H) + \nu$(CH)			
8	2957	ν(CH) + $\nu(N^+H)$			
9	2938	ν(C′H)		2927	
10	1738	$\nu(C{=}O_{acid})$	1746		1724
11	1676	$\nu(C{=}O_{amide}) + \nu$(CN)	1677	1682	1678
12	1641	$\delta_a(N^+H_3)$		1629	1648
13	1602	$\delta_a(N^+H_3)$		1611	1622
14	1593	δ_a(NH) + ν(CN) + $\nu(C{=}O_{amide})$ + ν(NC′)	1584	1531	1535
15	1486	$\omega(C'H_2) + \nu$(C′C) + ν(CO) + $\omega(CH_2)$	1487		
16	1472	$\delta_s(N^+H_3) + \omega(C'H_2)$		1480	1452
17	1443	$\delta(C'H_2)$	1434	1447	1437
18	1433	$\delta(CH_2) + \delta_s(N^+H_3)$	1434		1420
19	1408	$\omega(CH_2) + \delta(CH_2)$	1410	1399	1402
20	1362	δ(COH) + $\omega(C'H_2)$	1350		1362
21	1329	$t(CH_2) + \rho(N^+H_3)$	1308	1315	1307
22	1266	δ_s(NH) + ν(CO)	1265	1249	1249
23	1247	ν(CO) + $\omega(C'H_2)$ + δ(COH)			
24	1242	$t(C'H_2)$	1219	1242	1219
25	1188	ν(CN)			
26	1155	$\rho(N^+H_3) + \omega(CH_2) + t(CH_2)$	1135	1158	1130
27	1126	$t(CH_2) + \rho(N^+H_3)$	1117	1100	1090
28	1050	$\nu(N^+C)$	1040	1046	1032
29	1002	$\rho(C'H_2) + \gamma(CO_{acid})$	1013	1007	
30	985	ν(CC) + ν(C′C)		968	980
31	925	$\rho(CH_2) + \gamma(CO_{amide}) + \rho(N^+H_3)$		918	946
32	907	ν(CC′) + ν(CC)	903	910	
33	700	$\delta_a(CO_{amide}) + \delta$(NCC)	708	708	708
34	661	$\tau(CO_{acid}) + \gamma(CO_{acid}) + \rho(C'H_2)$	661	665	644
35	618	τ(CN) + $\gamma(CO_{amide})$ + γ(NH) + $\rho(CH_2)$			
36	594	$\delta_a(CO_{acid}) + \delta$(NC′C)		598	
37	568	$\delta_s(CO_{acid}) + \delta_a(CO_{amide})$		588	
38	537	$\gamma(CO_{amide}) + \gamma$(NH)		535	
39	508	$\gamma(CO_{acid}) + \tau$(CO)			
40	405	$\delta(N^+CC) + \delta_s(CO_{acid})$		396	
41	331	$\delta_s(CO_{amide}) + \delta_s(CO_{acid}) + \delta_a(CO_{amide})$		317	
42	269	δ(NC′C) + $\delta_a(CO_{acid})$		298	
43	196	τ(C′C) + τ(CC) + γ(NH) + $\tau(N^+C)$			
44	179	$\tau(N^+C) + \tau$(C′C)			
45	111	$\delta_s(NH_{amide}) + \delta_s(CO_{amide}) + t(CH_2)$			
46	89	τ(CC) + $\tau(N^+C)$			
47	79	τ(C′C) + τ(CN)			
48	40	τ(NC′) + γ(NH) + τ(CC)			

[a] Taken from ref. 19.

Conclusions

The fitting procedure to obtain the scale factors from the ab initio force field of GH has shown to be very successful, giving an average deviation of 9.7 cm^{-1} between the predicted and the experimental frequencies for seven isotopomers. These scale factors were used to predict the frequencies of GGH; the results were shown to be in good agreement with the experimental ones with an average deviation of 7.6 cm^{-1} for the smallest dipeptide hydrochloride. A complete set of nonredundant force constants was obtained for both GH and GGH. From the accuracy of the predicted frequencies it is clear that the methodology could, in principle, be used successfully for the prediction of vibrational frequencies and their force fields of larger polypeptides from their parent amino acids.

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Supporting Information Available: Tables listing optimized Cartesian coordinates obtained by using the 6-31G** basis set for the minimum energy conformation, local symmetry coordinates of GH and GGH and their nonredundant scaled force constants, internal coordinates, local symmetry coordinates, and fitted frequencies and their PEDs at both HF and MP2 levels of theory of acetic acid, and figures showing internal coordinates of GH and GGH, atom numberings of acetic acid, and a flow chart of the algorithm used for fitting (14 pages). Ordering information is given on any current masthead page.

References and Notes

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