layer allows charge transfer across the interface via electron tunneling. The cell thus has formally a semiconductor-oxide-redox couple system, resembling metal-insulator-semiconductor or metal-oxide-semiconductor cells, though the oxide thickness is much less than common in these.

Surface oxidation displaces surface states in the band gap so as to increase the energy gap between neighboring states, thus reducing the cross sections for nonradiative electron-hole recombination.[5] These cross sections, like other radiationless relaxation processes, depend on the energy gap between the initial and final states. The larger the gaps the smaller the cross sections, because removal of large amounts of energy by collision with phonons is unlikely. Recently, we reported that the performance of the p-InP/VCl_3-VCl_2-HCl/C cell was improved also by the chemisorption of submonolayer amounts of silver at specific sites on the p-InP surface.[6] The effects of both oxygen and silver on the surface of p-InP resemble the effect of chemisorption of a submonolayer of Ru^{3+} and Pb^{2+} on n-GaAs surfaces and grain boundaries. Strengthening of the bonds at n-GaAs surfaces by reaction with Ru^{3+} has been shown to reduce the recombination velocity.[5,20]

We also note that an oxide of submonolayer thickness was shown by Spicer et al.[11] to substantially shift the surface Fermi level from the proximity of the valence band maximum to that of the conduction band minimum and to change the spacings of the acceptor and donor surface states. In this light, the performance of the new cell appears to result from the conjunction of two favorable effects: (a) enhanced protection against photocorrosion of the surface, which in principle holds for all p-type semiconductors in photoelectrochemical solar cells; (b) chemical changes resulting in a redistribution of states of the (111) surface, reducing recombination, and thus favorable to efficient charge transfer. We interpret these latter modifications as resulting from the existence of a thin, surface oxide film. In the case of GaAs, the arsenic oxide containing phase reacts with GaAs to form elemental arsenic, a semimetal, at the GaAs/oxide interface.[21-26] The resulting surface contains electronic states associated with As at the surface, which reduce the energy gaps crossed in the steps of the radiationless recombination process and lead to a high surface recombination cross section that lowers the fill factor and the open circuit voltage.

7. Conclusions

Spectroscopic ellipsometry and low-energy ions scattering spectroscopy show that the (111)A (indium) face of p-InP consists of hydrated indium oxide. The thickness of this layer is 4 Å. Below this layer one finds, to a maximum depth of 10 Å, a mixture of two phases, hydrated indium oxide and indium phosphide. At depths exceeding 10 Å, one finds only pure InP. We attribute the low electron-hole recombination velocity at the p-InP-HCl interface to termination of the lattice without the generation of weak or "dangling" bonds that could give rise to states with high recombination cross sections.

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Vibrational Circular Dichroism in Amino Acids and Peptides. 4. Vibrational Analysis, Assignments, and Solution-Phase Raman Spectra of Deuterated Isotopomers of Alanine

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Abstract: The complete vibrational frequency assignments for alanine-d_0, alanine-C^*-d_1, alanine-C-d_3, alanine-C-d_4, and alanine-N-d_3 in aqueous solution are presented. The assignments are based primarily on solution-phase Raman spectra, with results of infrared and Raman solid-phase spectra, a Urey-Bradley normal coordinate analysis, and existing literature data also taken into consideration. The new spectra have led us to a self-consistent assignment, and, with the exception of a few modes where skeletal stretching and rocking motions are strongly mixed, the observed spectra may be interpreted well in terms of group frequencies and predominantly local motions. In this respect our results differ from previous investigations which postulate extensive vibrational coupling between all parts of the molecule. Results of this frequency assignment and vibrational analysis form the basis for the interpretation and calculation of the infrared vibrational circular dichroism spectra presented in the following papers.

Vibrational circular dichroism (VCD) spectra of amino acids and oligopeptides in aqueous solutions are of interest from both a theoretical and biophysical standpoint. VCD, and its companion technique, Raman optical activity, have recently begun to reveal sensitive structural and stereochemical details of molecules in solution,[2-5] and small peptides provide a closely related series of

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Table I. Hydrogen Stretching Frequencies in Wavenumbers of Alanine and Deuterium Isotopomers[a]

assigned mode	Ala-d_0		Ala-C^*-d_1		Ala-C-d_3		Ala-C-d_4		Ala-N-d_3	
	obsd	calcd	obsd	calcd	obsd	calcd	obsd	calcd	obsd	calcd
$\nu^a_{NH_3^+}$	3080[a]	3068	3080[b]	3068	3080[b]	3068	3080[b]	3068	2290[b]	2263
$\nu^a_{NH_3^+}$	3060[b]	3068	3060[b]	3068	3060[b]	3068	3060[b]	3068	2230[b]	2262
$\nu^s_{NH_3^+}$	3020[b]	3020	3020[b]	3018	3020[b]	3020	3020[b]	3018	2160[b]	2162
$\nu^a_{CH_3}$	3003[c]	2999	3008	2999	2251	2228	2256	2228	3003	2999
$\nu^a_{CH_3}$	2993	2998	2991	2998	2236	2226	2245	2226	2993	2998
ν_{C^*H}	2962[e]	2966	2210[d]	2170	2962	2964	2194	2170	2962[e]	2968
$\nu^s_{CH_3}$	2949	2946	2947	2949	2126	2116	2129	2114	2949	2946
$2\times\delta_{CH_3}$	2893		2888		2085/2075		2081		2893	

[a] Frequencies in Tables I–III are believed to be accurate to ±2 cm^{-1}. [b] Solid-state frequency (infrared and/or Raman). [c] Unresolved high-frequency shoulder. [d] A weak shoulder is also present at ~2190 cm^{-1}. [e] This frequency is transferred from alanine-C-d_3.

molecules for which solution-phase structural and conformational information would be highly useful. We have concentrated our initial efforts on the simplest optically active amino acids and peptides with the aim of carrying out detailed vibrational analyses and VCD calculations. In order to perform the requisite VCD calculations, accurate descriptions of nuclear displacements in the normal modes of vibrations are needed. However, for chiral peptide molecules, this information, or an accurate force field leading to this information, is currently unavailable in the literature.

Alanine, the simplest chiral amino acid, has been the subject of a number of vibrational studies over the last 25 years.[6-19] With one exception,[6] all spectral data of the prior studies were reported in the solid state in both infrared or Raman spectroscopy. These data, however, have proven unsatisfactory for the interpretation of VCD observed above 2000 cm^{-1} by these authors[20-23] in both aqueous solution and solid (mull) phases. In particular, the lack of C–H stretching data in all prior infrared work and some misassignments in the C–H deformation region, both caused by the relative insensitivity of solid-phase infrared spectroscopy toward these modes, prompted the authors to reinvestigate these spectral regions at the time when the first VCD results were reported, and some initial vibrational assignments and VCD intensity calculations were carried out using these preliminary vibrational data.[23]

In this paper we report a self-consistent detailed vibrational assignment of alanine and various isotopomers. These results are based mainly on solution (H_2O and D_2O) Raman spectra and solid-state Raman data obtained by us and recently by Byler and Susi.[17,18] Solid-state infrared data have also been obtained, but they do not exhibit as much detail as the corresponding Raman spectra, particularly in the frequency range above 2000 cm^{-1}. Nevertheless, we find that the agreement between solid-state Raman and infrared frequencies is very good in regions where the infrared spectra show good spectral quality. Wherever possible, our assignments and frequencies are based on the *solution*-phase Raman spectra since our ultimate aim is to interpret *solution*-phase VCD spectra. We have previously shown that the correspondence between Raman and VCD spectra is very good and that relatively complex VCD patterns resulting from overlapping infrared peaks can be assigned in detail with Raman solution data.[21]

Using our more accurate set of vibrational assignments and observed frequencies for alanine and several deuterium isotopomers, we have constructed a Urey–Bradley force field for the eventual purpose of calculating VCD intensities. The details of this force field together with a comparison of calculated to observed vibrational frequencies are presented below. In the following papers[24,25] we use this force field as the basis for the calculation of VCD intensities using first the fixed partial charge model[24] and subsequently the localized molecular orbital model[25] where detailed comparisons to new isotopic VCD spectra of alanine in the CH stretching region are made.

The vibrational spectra, assignments, and calculations of deuterated alanine isotopomers presented here comprise the first comprehensive *solution*-phase vibrational study of alanine. It is also the first isotopic study to include the lone α-hydrogen deuterated species (C^*-d_1), making possible unambiguous assignments in regions where misassignments or extensively mixed assignments are present in the current literature.

Experimental Section

N-Deuterated alanine isotopomers were preared by lypholizing the corresponding alanine species twice from D_2O. Alanine-C^*-d_1 was prepared by N-acetylation in D_2O, which yields racemic *N*-acetylalanine-C^*-d_1, and was subsequently resolved with acylase I.[26] Alanine-C-d_3 was purchased from Merck Sharp and Dohme, Ltd., Canada, but exhibited strong background scattering particularly in the solid state. Extraction of impurities in acetone and subsequent lypholization from H_2O/D_2O reduced the background to acceptable levels. Alanine-C-d_4 was also purchased from Merck Sharp and Dohme, Ltd., Canada, and was used without further purification. A medium-strong band at ca. 2400 cm^{-1} led us to believe that the sample was actually alanine-d_7; upon dissolving it in excess H_2O, mostly alanine-D-d_4 was obtained with only a remaining weak band at 2400 cm^{-1} due to residue HOD/D_2O.

Raman spectra were obtained using a completely digital Raman spectrometer at Hunter College, interfaced to a North Star, Inc., computer (Model HRZ-2-48) incorporating a Z-80A CPU, 48K of core and ca. 360K of on-line disk memory. The spectra reproduced in the following figures were obtained via a Hewlett–Packard digital plotter

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Table II. Hydrogen Deformation and Skeletal Stretching Frequencies in Wavenumbers of Alanine and Deuterium Isotopomers

mode assignment	Ala-d_0		Ala-C^*-d_1		Ala-C-d_3		Ala-C-d_4		Ala-N-d_3	
	obsd	calcd	obsd	calcd	obsd	calcd	obsd	calcd	obsd	calcd
$\delta^a_{NH_3^+}$	1645[a]	1635	1645[a]	1634	1645[a]	1635	1645[a]	1634	1190[a]	1186
$\delta^a_{NH_3^+}$	1625[a]	1633	1625[a]	1632	1625[c]	1633		1632	1180[a]	1170
$\nu^a_{CO_2^-}$	1607[b]	1610	1607[b]	1605	1607[b]	1610	1607[b]	1604	1607	1609
$\delta^s_{NH_3^+}$	1498[a]	1507	1498[a]	1505	1498[a]	1507	1495[a]	1505	1145[a]	1135
$\delta^a_{CH_3}$	1459	1462	1456	1462	1038	1050	1055[d]	1056	1461	1463
$\delta^a_{CH_3}$	1459	1463	1456	1461	1038	1050	1055[d]	1053	1461	1462
$\nu^s_{CO_2^-}$	1410	1405	1407	1404	1402	1405	1401	1404	1409	1405
$\delta^s_{CH_3}$	1375	1383	1373	1371	1050	1066	1055[d]	1070	1375	1382
δ_{C^*H}	1351	1349	959	975	1347	1355	947	968	1337	1345
δ_{C^*H}	1301	1294	880[c]	892	1291	1301	887[e]	893	1291	1296
$\zeta_{NH_3^+}$	1220	1191	1211	1263	1220	1187	1248	1256	874	896
$\zeta_{NH_3^+}$	1145	1155	1158	1174	1165	1147	1165	1170	840	849
ν^a_{CCN}	1110	1126	1079	1144	1109	1116	1110	1132	1148	1163
$\nu_{CC(O_2)}$	1001	1017	1010	1033	941	999	1015	1017	1097	1078
ζ_{CH_3}	995	964	1000 sh	958	820	791	823	779	1055	1045
ζ_{CH_3}	922	934	899[c]	934	758	747	751	743	920	937
ν^s_{CCN}	850	879	823	852	921	883	880[e]	856	812	798

[a] Solid-state Raman or infrared frequencies. [b] Solution frequency of alanine-N-d_3 in D_2O. Solid-state frequencies for the antisymmetric CO_2^- group are significantly lower: 1596, 1592, 1598, 1592, and 1591 cm^{-1} respectively for Ala-d_0, Ala-Cd_1, Ala-Cd_3, and Ala-Cd_4. [c] These modes are accidentally degenerate in solution, but clearly split in the solid phase. [d] Only one strong peak is observed in the CD_3 deformation region. [e] These modes are accidentally degenerate in solution, but are resolved in the solid-phase Raman spectra.

Table III. Heavy-Atom Deformation and Torsion Frequencies in Wavenumbers for Alanine and Deuterium Isotopomers

mode assignment	Ala-d_0		Ala-C^*-d_1		Ala-C-d_3		Ala-C-d_4		Ala-N-d_3	
	obsd	calcd	obsd	calcd	obsd	calcd	obsd	calcd	obsd	calcd
$\gamma_{CO_2^-}$	775	764	747	761		727		723	778	757
$\delta_{CO_2^-}$	640	656	635	645	610	619	610	613	613	634
$\zeta_{CO_2^-}$	527	519	520	514	509	498	520	495	513	493
$\tau_{NH_3^+}$	477	473		471	478	468	476	465	335	341
δ_{skel}	399	397		396	374	378	372	377	377	378
τ_{CH_3}	296	292		292	191	201		200	273	288
δ_{skel}	283	267		266	297	259	293	258	258	263
δ_{skel}	219	226		226	220	223		223	211	214
$\tau_{CO_2^-}$	184	192		191	184	185	187	185	184	187

(Model 7210) interfaced to the above computer. All spectra were excited by ca. 300 mW of argon ion radiation at 514.5 nm; data acquistion times of between 2 and 4 s/data point were employed and data points are spaced by 1 cm^{-1}. All spectra shown were recorded under a spectral bandpass of ca. 5 cm^{-1} and were subsequently smoothed by a nine-point cubic smoothing procedure.[27] Sample concentrations were ca. 1 M at isoelectronic pH (pD).

All force-field refinement calculations were carried out using the program FPERT by Schachtschneider, which was adapted to run on the time-sharing DEC-10 computer system at Syracuse University. Transformation from Urey–Bradley space into internal coordinate space was carried out using program UBZM by the same author.

Vibrational Frequency Assignments

In this section we present a detailed vibrational assignment of the solution-phase Raman spectra of alanine and several isotopomers. The aim of this assignment is to obtain an unambiguous basis for the normal coordinate analysis and VCD calculations to follow. In a molecule such as alanine, devoid of any overall symmetry, an accurate force field can best be obtained through a vibrational assignment of several isotopically substituted species where the assignment is maintained throughout all computational procedures. In previous attempts to calculate the force fields of alanine, relatively vague assignments were subsequently "verified" by the potential energy distribution obtained in the course of the normal coordinate analysis; frequently, the mixing of modes as produced by the calculations were utilized to interpret the spectral changes observed upon isotopic substitution. Such procedures, of course, may produce erroneous results since all calculations carried out to date have been highly indeterminate, either by choice of the force field or by the lack of vibrational data or assignments.[12]

The vibrational spectra to be discussed are shown in Figures 1–5 and summarized in Tables I–III. Observed as well as calculated frequencies are listed in the tables. The observed frequencies are obtained from solution data (except when otherwise noted) since the solid-state data are, in general, less suitable for a normal coordinate analysis.

Hydrogen (Deuterium) Stretching Region, 2000–4000 cm^{-1}. The unambiguous assignment of this spectral region is of the utmost importance for the interpretation of the VCD results of alanine and its isotopomers.[24,25] The vibrational modes due to the NH_3^+ moiety cannot be observed in aqueous solution, but available solid-state Raman, infrared, and VCD spectra allow a consistent assignment in this region. The two antisymmetric NH_3^+ stretching vibrations, the splitting of which may be amplified by solid-state effects (vide infra), occur at ca. 3080 and 3060 cm^{-1}, and the symmetric vibration occurs at ca. 3020 cm^{-1} (cf. Table I). These assignments are confirmed by peak positions in the solid-phase VCD spectra.[22] Solid-state Raman spectra exhibit the two antisymmetric modes weakly, but distinctly. Upon deuteration of the NH_3^+ group, a number of broad, poorly resolved peaks are observed in both solid-phase Raman and infrared spectra between 2000 and 2350 cm^{-1}. Based mainly upon our VCD data in this region,[17] we assign bands at 2290, 2230, and 2160 cm^{-1} to the three nitrogen–deuterium stretching modes. The increase in the splitting between antisymmetric and symmetric modes upon deuteration was observed and calculated in a number of different vibrational modes and is particularly pronounced in stretching vibrations, as evidenced in Table I.

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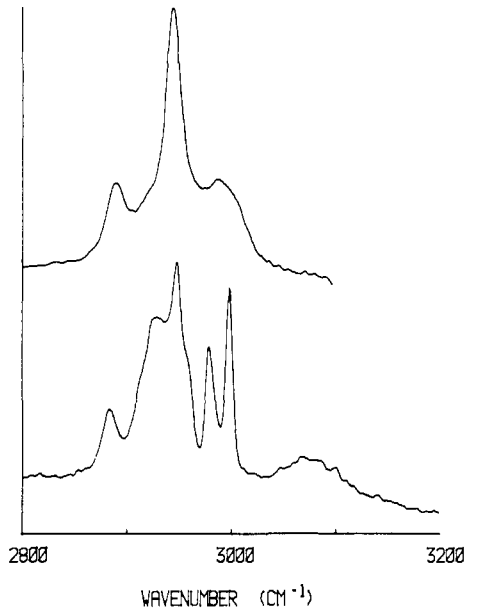

Figure 1. Raman spectra in the hydrogen-stretching region of alanine-d_0 as an aqueous solution (top) and in the solid phase (bottom). In the top spectrum, a strong water peak extending down to ca. 2900 cm^{-1} was digitally subtracted.

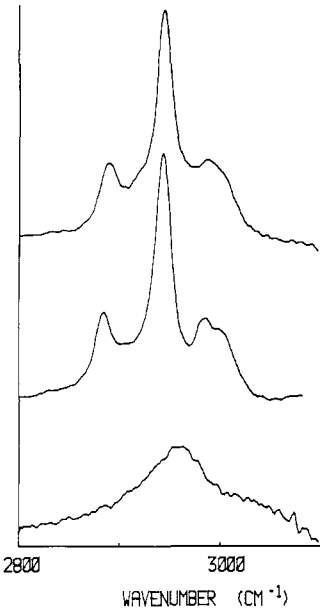

Figure 2. Raman spectra in the C–H stretching region of alanine-d_0 (top), alanine-C^*-d_1 (middle), and alanine-C-d_3 (bottom) as aqueous solutions. In all three spectra, the water background was subtracted and the intensities were scaled to compensate for concentration differences.

We next consider the C–H stretching region of alanine. In Figure 1 the Raman spectra of solid- and solution-phase alanine-d_0 in the 2800–3100-cm^{-1} region are compared. The intensity of the broad peak in the solid-state spectrum at ca. 2930 cm^{-1} depends on the crystalline structure and is different for solid DL- and L-alanine.[28] The solution spectrum displayed in Figure 1 was obtained by subtraction of a broad water background spectrum, which is a strong, featureless band that is somewhat more intense than the alanine C–H peaks at its maximum near 3100 cm^{-1}. The C–H stretching region of alanine-N-d_3 in D_2O is identical with that of alanine-d_0 if a D_2O background, extending from 2900 cm^{-1} to lower frequencies, is subtracted. Thus, one can be assured that the spectrum displayed in Figure 1 is, indeed, due to C–H vibrations only and that N–H overtones do not contribute to the observed band shape. This fact is important, since the VCD results of all isotopomers were obtained in D_2O solution.

Figure 2 shows the solution C–H stretching vibrations for alanine-d_0, alanine-C^*-d_1, and alanine-C-d_3 in H_2O. This spectral region is interpreted as follows. In the parent compound, the high-frequency band maximum at 2993 cm^{-1} shows a high-frequency shoulder as 3003 cm^{-1} which is actually resolved in alanine-C^*-d_1. Both peaks at 2993 and 3003 cm^{-1} are depolarized in the Raman spectrum and exhibit a distinct sigmoidal couplet in the VCD spectra.[24,25] Accordingly, we assign these modes to the near-degenerate antisymmetric stretching vibrations. The splitting of these modes must be considered carefully. Although the observed mode maxima are split by 10 cm^{-1}, curve analysis of both the infrared and Raman solution spectra shows[24] the individual modes to be split by slightly more than 20 cm^{-1}. This corresponds closely to the observed splitting in the solid state of just under 20 cm^{-1}. Although solution splittings of this magnitude may seem relatively large, the liquid-phase splitting of the methyl group in 1-bromo-1-chloro-1-fluoroethane has been observed[29] to be 19 cm^{-1} in its Raman spectrum, and thus the situation in alanine does not appear unrealistic.

The most prominent feature in the C–H stretching region is a very intense, highly polarized band at 2949 cm^{-1}. This band, present in alanine-C^*-d_1 and absent in alanine-C-d_3, is accordingly assigned to the methyl symmetric stretching mode. In alanine-C-d_3, only a broad band centered at 2962 cm^{-1} was observed superimposed on the water background. This observation suggests that the methyne stretching mode lies beneath the methyl symmetric stretching mode in alanine-d_0; indeed, the C–H spectral region of alanine seems to be a mere superposition of the spectra of alanine-C^*-d_1 and of alanine-C-d_3. The relatively intense peak at ca. 2890 cm^{-1}, present in all species containing a CH_3, is attributed to a Fermi resonance enhanced overtone of the methyl deformations at ca. 1460 cm^{-1}. In the solid phase a second overtone band appears at 2930 cm^{-1} in addition to one at 2886 cm^{-1} which corresponds to the solution band. The curve analysis referred to above reveals[24] a weak band at ~2915 in both the infrared and Raman indicating that in solution the high-frequency band is weaker (but present!) and that the overall splitting of these two overtone bands is reduced relative to the solid state. In the previously reported solid-state Raman spectra of alanine-C^*-d_1,[22] the intensity of the strong band at ca. 2950 cm^{-1} was attributed to the methyl symmetric vibration, which is in perfect agreement with out present solution data. Detailed inspection of this peak in alanine-d_0 in Figure 1 reveals a high-frequency deflection on this peak, which arises from the methyne peak at just slightly higher frequency. Thus, it appears that in both solution and solid phases, the methyne and symmetric methyl stretching peaks are close to one another and are nearly superimposed in the parent molecule.

The C–D stretching spectra of alanine-C^*-d_1, alanine-C-d_3, and alanine-C-d_4 in H_2O are shown in Figure 3. Obviously, the C–D spectrum in alanine-C-d_4 bears little resemblance to the corresponding spectrum of the perprotio compound. Comparison of Figure 2 and 3 reveals the increase in splitting between symmetric and antisymmetric modes upon deuteration. The assignment in this region is facilitated by Raman depolarization measurements which show that the high-frequency band at 2236 cm^{-1} is depolarized and exhibits a well-resolved second weaker peak at 2251 cm^{-1}; all other peaks between 2000 and 2300 cm^{-1} are highly polarized.[28] Accordingly, we assign the two peaks near 2235 and 2250 cm^{-1} in alanine-C-d_3 and alanine-C-d_4 to the near-degenerate CD_3 antisymmetric stretches, and the peak at 2126 cm^{-1} to the symmetric stretching motion. The methyne C–D stretching mode is a broad peak of medium intensity clearly observable in alanine-C^*-d_1 and alanine-C-d_4 at ca. 2200 cm^{-1}. There are, in addition, several strong lower frequency bands in the species with a deuterated methyl group. The two bands near 2080 cm^{-1} are assigned to overtones of the CD_3 antisymmetric deformations (~1040 cm^{-1}) and the low-frequency band shoulder at 2110 is

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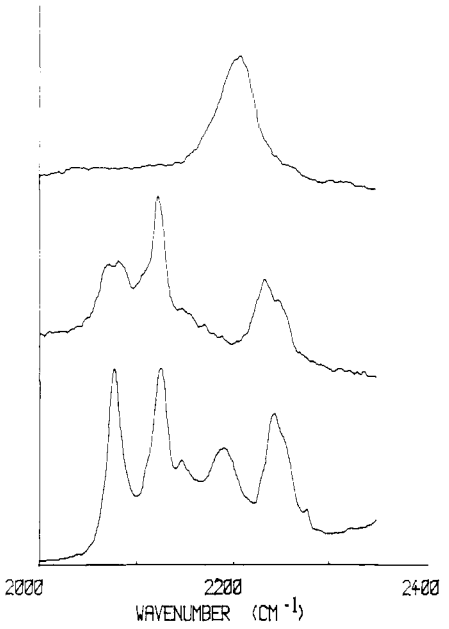

Figure 3. Raman spectra in the C–D stretching region of alanine-C^*-d_1 (top), alanine-C-d_3 (middle), and alanine-C-d_4 (C^*-d_1-C-d_3) (bottom) as aqueous solutions. The intensities are scaled to compensate for minor differences in solution concentration.

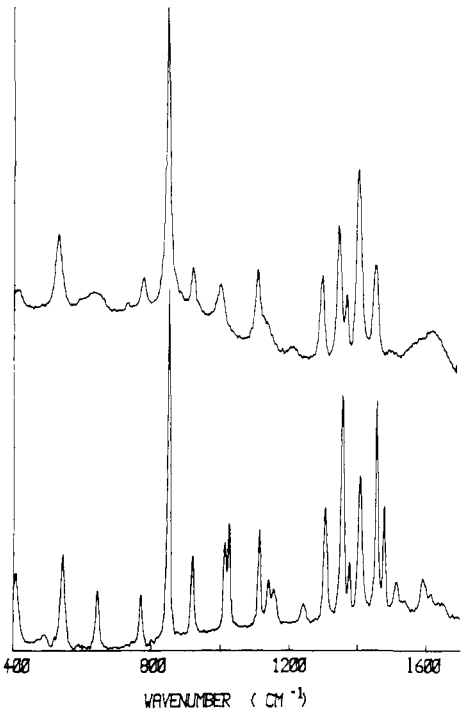

Figure 4. Raman spectra of alanine-d_0 as aqueous solution (top) and in the solid phase (bottom).

most likely the overtone of the symmetric CD_3 deformation ($\sim$ 1050 cm^{-1}).

The methyne stretching modes in alanine-C-d_3 (Figure 2) as well as in alanine-C^*-d_1 (Figure 3) are extremely broad peaks with a half-width in excess of 60 cm^{-1}, which is in contrast with the otherwise very narrow solution Raman bands in the carbon–hydrogen stretching region. In fact, close inspection of the C–D stretching peak in alanine-C^*-d_1 in Figure 3 reveals a low-intensity, low-frequency shoulder. This strongly suggests an association of alanine in concentrated solution. However, the methyne hydrogen is not a prime choice for the formation of a hydrogen bond from general chemical intuition. The only other broad solution bands are some of the low-frequency CO_2^- motions, which seem to be much better candidates for hydrogen bonding. This subject will be discussed later in this section as association in solution can perturb the vibrations of the single molecular species.

Hydrogen Deformation and Heavy-Atom Stretching Region, 700–1700 cm^{-1}. In the midfrequency region there exists some abiguity and contradiction about the assignments in the previous literature. We believe that our assignments, which are based on five isotopomers, will reduce this ambiguity significantly and simultaneously improve the basis for subsequent VCD calculations. The spectra to be discussed are displayed in Figures 4 and 5 and are summarized in Table II. Inspection of Figure 5 reveals that either methyne or amine deuteration produces significant changes in modes which are not immediately associated with the substitution center. Thus, a vibrational assignment has to be developed which takes into account this vibrational coupling. The interaction between vibrational modes initially makes the assignment of the modes difficult, but it eventually provides insight into the dynamics of the molecular vibrations, thus aiding the normal coordinate analysis. In Figure 4 we compare the aqueous solution- and solid-state Raman spectra of alanine-d_0 as an example of the utility of the solid-state spectra in identifying degenerate modes and distinguishing alanine bands from solvent bands.

In Figure 5 the vibrations above 1300 cm^{-1} may still be discussed, however, in terms of localized vibrations. The N–H deformations, like the N–H stretching vibrations, are very weak in the Raman spectrum and cannot be observed in aqueous solution. Solid-state infrared and Raman spectra indicate that the bands at 1645 and 1625 cm^{-1} are the antisymmetric and the band at ca. 1500 cm^{-1} the symmetric NH_3^+ deformations. Upon deuteration, these modes shift to ca. 1190, 1180, and 1145 cm^{-1}.

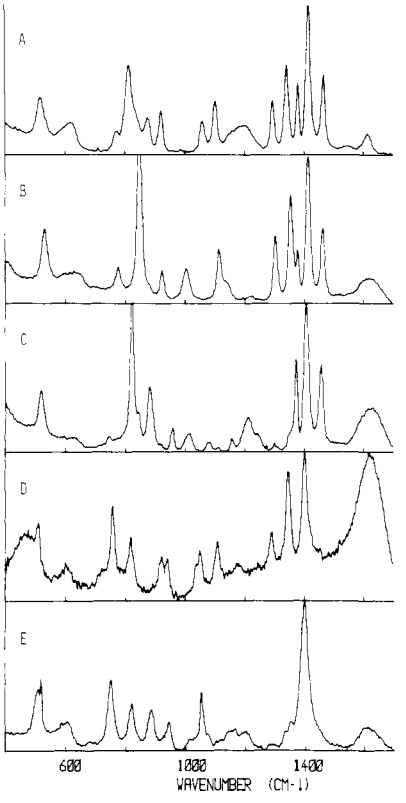

Figure 5. Solution Raman spectra of alanine and selected isotopomers: (A) alanine-N-d_3, ca. 1.8 M in D_2O; (B) alanine-d_0, ca. 1.8 M in H_2O; (C) alanine-C^*-d_1 ca. 1.8 M in H_2O; (D) alanine-C-d_3, ca. 0.4 M in H_2O; (E) alanine-C-d_4, (C^*-d_1-C-d_3), ca. 1.8 M in H_2O. All spectra are scaled to approximately equal intensity in the CO_2^- symmetric stretching band at ca. 1400 cm^{-1}.

The antisymmetric CO_2^- stretching mode can be observed in the solid state between 1588 and 1592 cm^{-1} for the different isotopomers and in solution at 1607 cm^{-1}. The corresponding symmetric stretching mode is a distinct band (and for some isotopomers the most intense Raman band) and occurs between 1400 and 1410 cm^{-1}. These CO_2^- modes maintain their vibrational

frequencies to better than a percent upon deuterium substitution and also perserve their relative intensities and band shape. We thus believe that these modes are well-localized vibrations for which group frequencies may be applied successfully.

We next turn to the methyl deformation modes. In the literature, controversy exists regarding the mixing of these modes with other vibrations of similar frequencies, notably the CO_2^- symmetric stretching and the methyne hydrogen deformation vibrations. Our results indicate that mixing between these modes occurs to a much lesser extent than previously assumed. The near-degenerate methyl antisymmetric deformation modes near 1460 cm^{-1} are not resolved in solution, but in the solid state, these two modes are seen at 1480 and 1465 cm^{-1} (cf. Figure 4). The methyl symmetric deformation mode appears at 1375 cm^{-1} in the parent molecule as a resolved high-frequency shoulder on a strong band due to methyne deformation motions. Upon N-deuteration, this shoulder becomes more distinct and better resolved, in both D_2O solution and the solid state. It is the methyl symmetric deformation which has produced the confusion in the earlier vibrational studies of alanine, since this band is hardly observable in the solid-phase infrared spectrum, and consequently, lower frequency bands were misassigned in search of the missing methyl mode. For instance, in the spectral region between 1200 and 1400 cm^{-1}, we disagree with the interpretation[19] of the ^{18}O data by Percy and Stenton since their assignment was entirely based on infrared spectra where the symmetric methyl deformation band is not included as an observed spectral feature.

Upon deuteration of the methyl group, the CD_3 deformation modes shift to between 1035 and 1055 cm^{-1}. The CD_3 deformations exhibit an interesting frequency inversion between the symmetric and antisymmetric vibrations. In the hydrogenated species, the antisymmetric components always occur at higher frequency, whereas the deuterated methyl group may or may not follow the same order. Comparing published CD_3 group frequencies it is apparent that the mass attached to the CD_3 group apparently causes this inversion.[30] CD_3F and CD_3CH_3 show the "expected" order, with the antisymmetric motions to the higher frequency, whereas in CD_3Cl, CD_3Br, and CD_3I frequency inversion has occurred with the symmetric deformation occurring at higher frequency. Accordingly, we assign the major peak at ca. 1050 cm^{-1} to the symmetric CD_3 and the unresolved should at 1038 cm^{-1} to the antisymmetric CD_3 deformations in agreement with the assignment by Byler and Susi.[17]

In all species containing the C*–H moiety, two strong band near 1350 and 1300 cm^{-1} appear which are assigned to the methyne deformation modes. In addition there is a third band at ca. 1110 cm^{-1} which exhibits major changes upon deuteration at the methyne position. This mode is assigned as one of the heavy-atom stretching vibrations (vide infra) which apparently drops significantly in intensity upon deuteration of the C–H group, since only very weak bands are observed in alanine-C^*-d_1 and alanine-C-d_4 around 1110 cm^{-1}. In these molecules the C*–D deformation modes occur near 950 and 880 cm^{-1}; cf. Table II.

The region from 1250 to 800 cm^{-1} (in the parent molecule) contains the NH_3^+ and CH_3 rocking modes and the three skeletal stretching motions. We favor the approach published earlier[7,8] of defining a symmetric and an antisymmetric CCN stretching coordinate, since the H_3C–CH–NH_3^+ group is a structural and mass analogue of an isopropyl group. In terms of a symmetric and antisymmetric CCN vibrations, the sensitivity of a number of vibrations toward deuteration may be understood, in particular, the sensitivity of the strong symmetric band at 850 cm^{-1} (in the parent molecule) toward both methyl and amine group deuteration.

In agreement with the solid-state assignment by Byler and Susi,[17,18] we assign the weak band observed in the solution spectrum of alanine-d_0 at 1200 cm^{-1} to the higher frequency NH_3^+ rock. The mode is sensitive to methyl and methyne deuteration and shifts to 1211 cm^{-1} in alanine-C^*-d_1, and to 1248 cm^{-1} in alanine-C-d_4. A shoulder or weak band between 1140 and 1170 cm^{-1} is assigned to the low-frequency rock of the NH_3^+ group. Upon nitrogen deuteration, these vibrations shift to 874 and 840 cm^{-1}, and mix with the symmetric skeletal stretch at 812 cm^{-1}.

The C–C bond stretching vibration between the asymmetric carbon and the carboxylic acid carbon is assigned to a band which is fairly prominent in alanine and alanine-C-d_3 at ca. 1110 cm^{-1}, but which becomes much less intense in alanine-C^*-d_1 and -C-d_4. This band shifts to ca. 1148 cm^{-1} upon nitrogen deuteration. A similar frequency shift is observed for the antisymmetric CCN stretching vibration, which occurs at 1001 cm^{-1} in the parent molecule and shifts to 1097 in alanine-N-d_3.

A detailed analysis of the isotopic spectral data has led us to the following assignment of the methyl rocking modes. In alanine and alanine-C^*-d_1, the rocking modes occur near 1000 and 900 cm^{-1}. Nitrogen deuteration shifts the higher frequency methyl rock to about 1050 cm^{-1}. For the CD_3 group, the rocking vibrations are observed near 820 and 750 cm^{-1}.

It is worth stressing at this point that the skeletal stretching motions involving the C*–C(methyl), C*–C(carboxylic), and C–N bonds still mix heavily with one another and to a lesser extent with the CH_3 and NH_3^+ rocking modes. Our view regarding the assignments described above and as listed in Table II is that they are most accurate for alanine-d_0 and that the principal character of various modes can be followed as they become deuterated and shift to lower frequency. Nevertheless, as modes move to lower frequency, particularly the modes assigned as δ_{C^*D}, δ_{CD_3}, and $\delta_{ND_3^+}$, they mix with the resident C–C and C–N stretching modes and alter to some extent the character of the vibrations between 800 and 1100 cm^{-1}. This conclusion follows directly from the variability of this region in Figure 5.

Heavy-Atom Deformation and Torsional Region, 100–800 cm^{-1}. Between 500 and 750 cm^{-1}, three distinct bands, attributed to the CO_2^- group, are observed in both the solid phase and solution. The CO_2^- wagging vibration is assigned to a band at 775 cm^{-1} in the parent molecule. This band and the CO_2^- rocking mode at 527 cm^{-1} are sharp in both the solid-state and solution spectra. The third mode, however, the CO_2^- deformation, becomes very broad in solution (cf. Figure 4). In fact, this band may even have a low-frequency shoulder, possibly resulting from association in solution. It was pointed out before that the C–H stretching vibration exhibits similar behavior in solution. Thus, initial attempts were made to study the shapes of these particular bands as a function of alanine concentration. Initial results, obtained over a concentration range from ca. 1.5 M to 0.03 M, however, have not resulted in observable changes although some other bands have shown significant sensitivity to concentration effects, notably the NH_3^+ torsion (vide infra). This subject is of considerable interest, since it may help to clarify the problem of solution/solvent interaction of highly charged species in water. Studies of the C–D vibration of alanine-C-d_1 are presently being pursued to help establish whether or not significant association does exist in aqueous solution.

The three torsional modes were assigned as follows: the 477-cm^{-1} band to the amine torsion, the 258-cm^{-1} band to the CH_3, and the 184-cm^{-1} band to the CO_2^- torsion. Three bands at 399, 396, and 211 cm^{-1} were assigned to the skeletal deformations.

Urey–Bradley Force-Field Calculations

The molecular geometry assumed for our calculations is the same as that used by Byler and Susi.[17,18] Their structural data in turn was based on a neutron diffraction study of crystalline alanine.[31] Minor variations in bond lengths of similar bonds (i.e., the three C–H bonds in the methyl group) have been suppressed, not only for simplicity, but since our calculations address alanine in the solution phase where more equivalence among bond lengths and bond angles is expected. Byler and Susi also used these averaged values in order to achieve greater transferability of their resulting force-field parameters for different amino acids. The neutron diffraction data[31] determine the location of hydrogen to

(30) Shimanouchi, T. "Tables of Molecular Vibrational Frequencies Consolidated"; National Bureau of Standards: Washington, D. C., 1972.

(31) Lehmann, M. S.; Koetzle, T. F.; Hamilton, W. C. *J. Am. Chem. Soc.* **1972**, *94*, 2657.

a high degree of precision as well as provide more refined values for the heavier atoms compared to earlier X-ray studies.[32,33]

The alanine geometry has tetrahedral angles about the methyl carbon, the α carbon, and the amine nitrogen. The methyl and amine functions are each staggered with respect to the remaining molecular frame, and no distinguishable rotameric forms need to be considered. The only significant variable to our calculations is the torsional angle of the carboxylic acid group relative to the rest of the molecule. Here we follow the crystal data which show one of the oxygens close to one of the amine hydrogens and the other oxygen close, but not as close, to the α hydrogen. This leaves two methyl hydrogens closer to the CO_2^- moiety than the remaining one which is essentially trans to it. Stereoprojections of our assumed conformation of alanine are provided in the following two papers. In the absence of any solution-phase structural data, we feel that theoretical calculations involving other conformations of the carboxylic group are not called for at this time.

For the calculation of vibrational normal coordinates in asymmetric molecules, several different approaches are possible. Standard general valence force field (GVFF) calculations may be attempted, but even in the most fortuitous situation (i.e., if a large number of isotopic frequencies are available) a large number of interaction force constants have to be arbitrarily set to zero. Use of a GVFF produces fairly accurate vibrational eigenvalues, but the uniqueness of the force field is questionable because of the large degree of indeterminancy.

A more promising approach utilizes only the off-diagonal force constants which lie fairly close to the diagonal of the **F** matrix; i.e., interaction force constants within a locally symmetric group are utilized. This approach was favored by Byler and Susi,[17,18] who used local symmetry force constants derived from typical GVFF diagonal and selected interaction force constants, and neglected all but a few interactions between different symmetry coordinates. This approach yields a force field of manageable size, but there still persists some ambiguity in the choice of the interactions between the symmetry coordinates. We feel that some of the calculated mixing between CO_2^- stretching and CH_3 and C–H deformation coordinates in Byler's work is due to the choice of the force field and is in disagreement with spectral evidence which points toward fairly unperturbed group frequencies in the 1200–1600-cm^{-1} range in alanine. Overall, however, the work by Byler and Susi provides the first sound basis for a vibrational assignment, both from an experimental and interpretational viewpoint.

The Urey–Bradley approach, which we utilized in previous efforts to study normal vibrations in asymmetric molecules (HCFClBr and $CH_3CFClBr$)[29] avoids the situation of neglecting off-diagonal force constants, but rather combines interaction force constants into fewer "nonbonded" interaction constants, for which good literature trial values exist. The difficulty in the Urey–Bradley approach lies in the fact that, even with good trial values, meaningless force constants may result from a perturbation process. This is due to the redundancy between diagonal deformation and nonbonded interaction constants for one and the same displacement coordinates; thus, a poor trial value in one of the force constants may be compensated by an even poorer refinement value of another force constant. This is particularly true in large molecules such as alanine, if strong mixing of coordinates is allowed.

To avoid such failures, we first refined force constants for locally symmetric portions of the molecules entirely separated from the rest of the molecule. In the case of the CH_3 (CD_3) group, for example, we utilized the complete kinetic energy matrices of alanine and alanine-d_3, but entered only six force constants, namely the C–C and C–H stretching, the diagonal CCH and HCH deformation, and the C···H and H···H nonbonded interaction constants. These force constants were subsequently refined using the isotopic data available, and the procedure was repeated for the NH_3^+ [ND_3^+], CO_2^-, and H–C*C(C)(N) [D–C*C(C)(N)] moieties. This approach yielded a set of trial force constants in good agreement with literature data which was subsequently refined for the entire molecule and three isotopomers. ^{18}O data, although available, were not utilized for two reasons; namely, they represent solid-state results and they do not report the frequency of the 1375-cm^{-1} band as mentioned above.

The calculated frequencies listed in Tables I–III were obtained from the perturbation optimized (FPERT) Urey–Bradley force field for the isotopic species alanine-d_0, -C*-d_1, -C-d_3, and -N-d_3 using the observed frequencies listed in the tables. The final set of optimized force constants is given in Table IV. The agreement between calculated and observed frequencies is very good except for the region between 800 and 1100 cm^{-1} where, as discussed above, extensive mixing in the deuterium-substituted species

Table IV. Definitions and Values of Urey–Bradley Force Constants for Alanine and Deuterated Isotopomers

no.	definition	value[a]	no.	definition	value[a]
1	C_O–O	7.355	20	CO_2^- wag	0.529
2	C*–C_O	3.010	21	CO_2^- τ	0.065
3	C*–H	4.101	22	CH_3 τ	0.017
4	C*–C_M	1.800	23	NH_3 τ	0.044
5	C*–N	2.500	24	O···C_O···O	3.184
6	N–H	4.778	25	C*···C_O···O	1.075
7	C_M–H	4.553	26	H···C*···C_O	0.580
8	C*–C_O–O	0.219	27	H···C*···N	0.499
9	O–C_O–O	0.130	28	H···C*···C_M	0.490
10	H–C–C_O	0.398	29	N···C*···C_O	0.387
11	H–C*–N	0.353	30	C_O···C*···C_M	0.264
12	H–C*–C_M	0.368	31	N···C*···C_M	0.778
13	N–C*–C_O	0.500	32	C*···N···H	0.617
14	C_O–C*–C_M	0.500	33	H···N···H	0.075
15	N–C*–C_M	0.720	34	C*···C_M···H	0.435
16	C*–N–H	0.418	35	H···C_M···H	0.100
17	H–N–H	0.575	36	ρ(C*)	0.053
18	C*–C_M–H	0.330	37	ρ(C_M)	0.008
19	H–C_M–H	0.487	38	ρ(N)	0.079

[a] Stretching (1–7) and nonbonded interaction (24–35) force constants are given in units of mdyn/Å; bending, wagging, torsion (8–23), and the intermolecular tension (36–38) force constants are expressed in units of mdyn/radian.

Table V. Calculated Potential Energy Distribution (PED) of the Normal Modes in Alanine-d_0

mode	PED[a]	mode	PED[a]
$\nu^a NH_3^+$	6 (93)	δ_{C*H}	11 (22), 12 (22), 27 (14), 28 (14)
$\nu^a NH_3^+$	6 (93)	$\rho_{NH_3^+}$	16 (14), 26 (11), 32 (13)
$\nu^s NH_3^+$	6 (88)	$\rho_{NH_3^+}$	16 (34), 32 (29)
$\nu^a CH_3$	7 (93)	$\nu^a CCN$	5 (21), 16 (12), 32 (18)
$\nu^a CH_3$	7 (94)	$\nu_{C-C(O_2)}$	2 (11), 16 (19), 18 (12), 32 (17), 34 (11)
ν_{C*H}	3 (68), 7 (6)	ρ_{CH_3}	18 (24), 34 (24)
		ρ_{CH_3}	18 (37), 34 (31)
$\nu^s CH_3$	3 (13), 7 (77)	$\nu^s CCN$	4 (16), 24 (10), 34 (15)
$\delta^a NH_3^+$	17 (82)	$\gamma_{CO_2^-}$	20 (60)
$\delta^a NH_3^+$	17 (83)	$\delta_{CO_2^-}$	24 (31), 25 (24)
$\nu^a CO_2^-$	1 (89)	$\rho_{CO_2^-}$	15 (13), 25 (29), 31 (20)
$\delta^s NH_3^+$	16 (32), 17 (45), 32 (22)	τ_{NH_3}	23 (90)
$\delta^a CH_3$	19 (83)	δ_{skel}	15 (25), 25 (22), 31 (21)
$\delta^a CH_3$	19 (85)	τ_{CH_3}	22 (80)
$\nu^s CO_2^-$	1 (54), 2 (18), 24 (18)	δ_{skel}	14 (30), 22 (14), 30 (18)
$\delta^s CH_3$	18 (21), 19 (31), 34 (14)	δ_{skel}	13 (30), 14 (12), 25 (17), 29 (21)

[a] Listed are the force constant numbers (see Table IV) followed by the percent contribution to the potential energy. Only force constants contributing 10% or more are shown.

(32) Simpson, H. J.; Marsh, R. E. *Acta Crystallogr.* **1966**, *21*, 550.
(33) Dunitz, J. D.; Ryan, R. R. *Acta Crystallogr.* **1966**, *20*, 617.

complicates the pattern originally present for alanine-d_0.

In Table V we present the potential energy distribution (PED) among the force constants for each of the vibrational modes of alanine-d_0. Only force constants participating by greater than 10% in the PED of a given mode are shown. From this we see hardly any mixing beyond the functional group vibration for all modes above ν^a_{CN}. Furthermore, the methyl rocking modes, the CO_2^- modes, and the torsion modes are clearly identified, leaving only the skeletal stretching and bending modes to remain extensively mixed. These results agree with our previously deduced assignments based on the isotopic Raman spectra. The mode assigned to ν^a_{CCN} is primarily C-N stretch but there is also a 5% PED contribution due to the $C-C_M$ stretch; the internal coordinate composition of this mode shows a $C-C_M$ stretching motion out of phase with, and 58% of the magnitude of, the C-N stretch. This mode also naturally couples with NH_3^+ bending motion. The $\nu_{C(CO_2)}$ mode has very little $C-C_M$ or C-N character but mixes with both methyl and amine bending modes. Finally the ν^s_{CCN} mode is predominantly $C-C_M$ stretch and methyl bend, but the C-N and $C-C(O_2)$ stretches contribute in phase with amplitudes of 58 and 29% of the $C-C_M$ motion. The ν^s_{CCN} mode can be regarded as a skeletal breathing mode which is consistent with its large effect on the polarizability and hence is striking Raman intensity. This simple pattern for the stretching modes is disrupted by methyl and amine deuteration when both their deformation and rocking modes mix extensively with the skeletal stretches and with each other. Deuteration of the α position also disrupts the alanine-d_0 pattern, but to a lesser extent, and leaves the strong breathing mode essentially intact.

As a final point we wish to stress that although the force field for alanine was initially assembled from force-field descriptions of local symmetric regions as described above, this process should be regarded only as an efficient *means* of obtaining a zeroth-order field sufficiently accurate that FPERT could be applied effectively. The final force field has the same degree of intramolecular interaction that would be obtained if a whole molecule approach to the zeroth-order force field were used, provided that the same set of nonzero force constants was employed in both approaches.

Conclusions

The vibrational assignments and the Urey-Bradley force field presented here meet our objective of providing a good description of the vibrational modes of deuterated alanine isotopomers in solution. This force field provides a good foundation within the harmonic approximation for the calculation of vibrational circular dichroism intensities. With the Raman spectra of deuterated isotopic species representing selective deuteration of the three hydrogen-bearing substituents of alanine, CH_3, C*H, and NH_3^+, we have been able to make unambiguous assignments for all vibrational regions, excepting the obviously mixed region from 800 to 1100 cm^{-1}. We can now proceed to VCD calculations in CH stretching region, where spectral data are available, without concern that our lower frequency motions are improperly described, thereby distorting our results. This is not an idle concern, since to a certain degree all internal coordinate motions contribute to each normal mode in an asymmetric molecule and VCD is more sensitive to distant motions within a molecule than ordinary infrared absorption. In addition, this new force field should also provide a good basis for the calculation of mid-infrared VCD for alanine and related molecules when experimental data in this region become available.

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Registry No. Ala-d_0, 56-41-7; Ala-C^*-d_1, 21386-65-2; Ala-C-d_3, 63546-27-0; Ala-C-d_4, 18806-29-6; Ala-N-d_3, 19470-97-4.

Vibrational Circular Dichroism in Amino Acids and Peptides. 5. Carbon-Hydrogen Stretching Vibrational Circular Dichroism and Fixed Partial Charge Calculations for Deuterated Isotopomers of Alanine

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Abstract: Vibrational circular dichroism (VCD) in the CH stretching region for alanine-N-d_3, alanine-C^*-d_1-N-d_3, and alanine-C-d_3-N-d_3 are presented and empirically analyzed. It is shown that selective deuteration in alanine reveals direct insights into the origin of VCD intensity and vibrational coupling between the methyl and methyne substituents. By employing spectral curve analysis to the alanine CH absorption spectra, the frequencies, bandwidths, and intensities of overlapping vibrational bands were determined revealing the presence of several combination and overtone bands in addition to the expected four fundamentals. Analysis of two of the overtones with Fermi resonance methods yielded a revised set of observed frequencies for the fundamentals which in turn led to a refined Urey-Bradley description of these modes. Finally VCD intensities were calculated with the fixed partial charge model and compared with experiment. Conclusion regarding the limitations of the FPC model for alanine VCD calculations are discussed.

Vibrational circular dichroism[2-6] (VCD) has emerged over the past half-decade as a new spectroscopic probe of structure, conformation, and configuration of small chiral molecules and helical polymers in solution. Parallel developments in the related field,

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