involved in π double bonds, is under investigation.

5. Conclusion

From these results, a significant energetic separation between the $^{2}A''$ and $^{2}A'$ ionic states is evidenced for both phosphaethene and 2-phosphapropene. This should lead for these compounds to an enhanced reactivity of the P═C double bond as compared with the phosphorus lone pair toward transition metals (η^2 P═C bonded complexes[26]). To our knowledge, the behavior of phosphaalkenes toward complexation has been achieved only on heavily substituted compounds,[27] and no experimental data on the ability of phosphaethene to form either η^1 or η^2 complex are available. Further photoelectronic studies on substituted phosphaalkenes are under investigation in order to complete these results.

Acknowledgment. We thank Mrs Maryse Simon for her efficient technical assistance during the course of this work. This project is financially supported by the CNRS (ATP: Synthetic processes under extreme physical conditions).

Registry No. 1, 61183-53-7; **2**, 107257-40-9.

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Infrared Vibrational Circular Dichroism of Alanine in the Midinfrared Region: Isotopic Effects

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Abstract: The infrared vibrational circular dichroism (VCD) spectra of L-alanine (L-Ala) and L-alanine-N-d_3 (L-Ala-N-d_3) in water and deuteroxide are reported between 900 and 1700 cm^{-1}. Large VCD signals are observed in vibrations associated with the C–H deformation modes of the methine hydrogen, whereas the other vibrations exhibit small, but certainly observable, VCD. The methine deformation vibrations do change significantly upon N-deuteriation of the molecule, both in terms of their frequencies and vibrational and VCD intensities.

Infrared (vibrational) circular dichroism, the differential absorption of left and right circularly polarized infrared radiation by molecular vibrational transitions, has recently been used by a number of researchers as a new probe for peptide and nucleotide conformation.[1-3] So far, conformational sensitivity for peptides was established in the amide I and amide II (1550–1700 cm^{-1}) spectral region in peptides,[2,3] and in the same wavenumber range in a number of model polynucleotides.[1] In the former case, the interaction of peptide linkages gives rise to distinct positive/negative couplets, which can, in principle, be related to conformation via the coupled oscillator model. Similarly, the interaction of certain base vibrations in the nucleotides produces pronounced couplets, which are indicative of the orientation of the coupling dipoles.

For very small peptides, such as dipeptides, we have shown recently[4] that the amide I and II vibrations do not produce significant VCD intensities, thus giving further evidence that the VCD intensities observed in large peptides are due to a coupling mechanism. However, we found very large VCD intensities[4] in the amide III spectral region (1270–1330 cm^{-1}). This region was previously studied in detail via investigation of the vibrational spectra of six isotopically substituted alanine dipeptides, and it was established that the "amide III" vibration is a delocalized, coupled vibration of an N–H deformation and adjacent C–H deformations.[5]

Although this vibrational study explains the observed VCD in terms of the vibrations involved, there is, to date, no explanation for the large intensity observed in the amide III region. A coupled oscillator or a simple fixed partial charge model calculation yields for the C*–H stretching or deformation vibrations, or the coupled amide III mode, VCD intensities that are about one order of magnitude lower than the observed values.[6a] Thus, the origin of the large intensity has to be investigated further. In the following paper, we report the VCD results of the monomeric molecule, alanine, between 800 and 1700 cm^{-1} in aqueous solution, with special emphasis on the C–H deformation region (1250–1350 cm^{-1}), to shed light on the origin of the large VCD intensities in these modes.

Both alanine and alanine-N-d_3 in H$_2$O and D$_2$O, respectively, were investigated. For both species, the VCD spectra are dominated by signals due to the methine C–H deformation vibrations, which exhibit very large VCD intensities in both species, whereas the remaining vibrations exhibit much smaller VCD intensities. This behavior is similar to the one observed in alanine in the C–H *stretching* range,[6] where the only large signal is due to the methine stretching vibration, at 2950 cm^{-1}. It was this large intensity of the methine stretching vibration in alanine, and all other α-amino

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acids and related molecules, which has led Nafie and co-workers[7] to the postulation of the ring current model.

The results of this work suggest that similarly enhanced intensities also exist for the methine deformation modes and, possibly, the amide III vibrations, since all other vibrational modes in the 900–1700 cm^{-1} region exhibit much smaller VCD intensities.

Finally, this is the first observation ever of VCD in aqueous solution below 1200 cm^{-1}. The data collected from solution in deuteroxide actually cover the range down to 900 cm^{-1}. This spectral range involves the skeletal vibrations, which for the first time are accessible from aqueous solutions. It should be pointed out that until a decade or so ago, it was considered impractical to even obtain standard infrared spectra from aqueous solutions, because of the high background absorbance of aqueous solutions. Now, it is possible to obtain high-quality infrared circular dichroism on these systems. With D_2O as solvent, and appropriate sample cell materials (vide infra), VCD of aqueous solutions should be accessible to 800 cm^{-1}.

Experimental Section

D- and L-alanine were obtained from Sigma Chemical Corp. and recrystallized from water, since both enantiomers contained impurities. N-Deuteriation was accomplished by a single lyophilization of the recrystallized material from D_2O. Flash evaporation often resulted in a deuteriated form as a yellow oil, with undesirable qualities. N-Deuteriated alanine was examined for impurities via NMR spectroscopy; no impurities could be found in the samples used for spectroscopic studies. The precise isotopic purity of alanine-*N*-d_3 is not known. However, since the infrared spectrum is very sensitive to the presence of O–H and N–H bonds, and no vibrations due to these groups were found, it is believed that the isotopic purity is better than 98%.

Infrared data were obtained on the VCD instrument (vide infra), or via a Beckman 4220 infrared spectrophotometer, interfaced to a laboratory computer, allowing for signal averaging and digital data manipulation. These data are accurate to ±1 cm^{-1}. Raman data referred to in this paper, and the instrumentation used for their collection, were reported previously.[5]

The Hunter College dispersive VCD instrument has been described in detail.[8] It allows spectral data in both H_2O and D_2O solutions to be collected down to the cutoff frequencies of the solvents, which are 1000 and 800 cm^{-1}, respectively. In the spectral range above 1250 cm^{-1}, CaF_2 was used for the sample cell, and BaF_2 below 1250 cm^{-1}. Sample concentration ranged from 0.2 to 1.75 M, as indicated in the figure captions. A path length of 15 μm, determined by a Teflon spacer, was used in all spectra. All spectra are corrected with a base line derived from both enantiomeric spectra. This base line is absorption independent and contains a few weak features between 1400 and 1600 cm^{-1} due to atmospheric water bands. The base line can be reproduced very well by collecting the VCD spectrum of the pure solvent.

Contrary to most VCD spectra reported to date, the VCD data obtained from the Hunter College apparatus are not calibrated via the reported procedure involving a second polarizer and a multiple retardation plate.[9] This is because a digital normalization of the VCD magnitude with respect to the total transmitted signal is performed,[8] and consequently, the magnitude of the VCD data is defined unambiguously. However, there is a constant intensity ratio of about 1.2 between data observed on Fourier Transform (FT) VCD instruments and the Hunter College unit (cf. the paper by T. B. Freedman immediately following this paper). These differences are most likely due to the somewhat better resolution of the FT experiment, particularly above 1300 cm^{-1}. Low resolution may cause cancellation of signals with opposite signs, and thus reduce the apparent VCD intensity.

Results and Discussion

The data for alanine and alanine-*N*-d_3 are presented in order from high to lower frequencies. Figure 1 shows the 1500–1700 cm^{-1} region of the deuteriated molecule in D_2O. This region is, of course, inaccessible in normal water due to the strong deformation vibration which masks the area between 1550 and 1700 cm^{-1}. The only vibration observed in the IR spectrum in this region is the antisymmetric stretching mode of the $-CO_2^-$ moiety, which occurs at 1623 cm^{-1}. This vibration shows small VCD intensities with $\Delta A/A$ of 1.1×10^{-5}. In areas of moderate solvent absorption, such small signals can be measured with ease in bands with relatively large infrared absorptions. This signal is analogous to that of the corresponding vibration in the alanyl dipeptide L-Ala-L-Ala and D-Ala-L-Ala, where the stereochemistry of the C-terminal alanine residue determines the sign of the $-CO_2^-$ antisymmetric stretching mode.[4] The shape of the infrared peak at 1623 cm^{-1} is nearly perfectly symmetric and exhibits a symmetric VCD curve at the same frequency. These observations indicate that there is one predominant conformation of the carboxylate group.

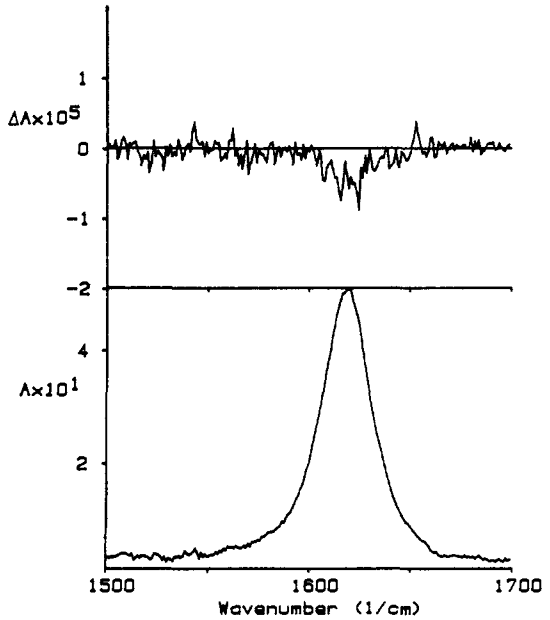

Figure 1. Infrared (bottom) and infrared VCD (top) spectra of L-Ala-*N*-d_3, 1500–1700 cm^{-1}: concentration, 0.2 M; path length, 15 μm; time constant, 1 s; band-pass, 8 cm^{-1}; 8 scans averaged; no smoothing.

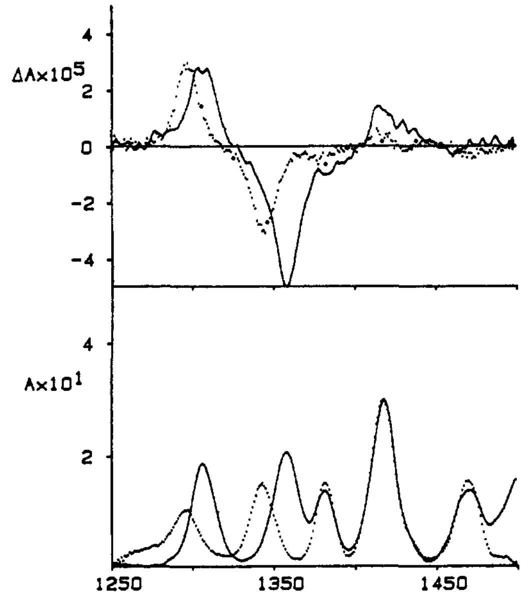

Figure 2. Infrared (bottom) and infrared VCD (top) spectra of L-Ala (solid) and L-Ala-*N*-d_3 (dotted), 1250–1500 cm^{-1}: concentration, 1.2 M; path length, 15 μm; time constant, 1 s; band-pass, 6 cm^{-1}; 6 scans averaged; no smoothing.

Figure 2 shows the solution infrared and VCD data of L-Ala and L-Ala-*N*-d_3 in the 1250–1500 cm^{-1} range. This region contains the methyl symmetric and antisymmetric deformations, the carboxylate symmetric stretching, as well as the methine defor-

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Table I. Vibrational Frequencies, Infrared and VCD Intensities, and Assignments of L-Ala and L-Ala-N-d_3

L-Ala			L-Ala-N-d_3			
freq[d]	$10^5\epsilon$[e]	$10^5(\Delta\epsilon/\epsilon)$[e]	freq[d]	$10^5\epsilon$[e]	$10^5(\Delta\epsilon/\epsilon)$[e]	assignment
			1623	1690	−1.1	ν^{as} ($-CO_2^-$)
1471	71		1470	89		δ^{as} ($-CH_3$)
1418	162	5.2	1417	167		ν^{s} ($-CO_2^-$)
1381	72		1381	84		δ^{s} ($-CH_3$)
1358	111	−27	1343	84	−22	δ (C*–H)
1306	100	16	1295	59	29	δ (C*–H)
1221	29	5.3				ρ ($-NH_3^+$)
1139	36	−4.2				ρ ($-NH_3^+$)
1117	63	−4.7	1148[c]			ν^{as} (CCN)[a]
1001	14		1103	30	−7.4	ν (C*–C)[b]
995[c]			1060	16		ρ (CH_3)
			918	18	9.8	ρ (CH_3)
			840[c]			ρ (NH_3^+)

[a] CH_3–C–NH_3^+, cf. text. [b] C*–CO_2^-. [c] Raman frequencies. [d] cm^{-1}. [e] L/(mol·cm).

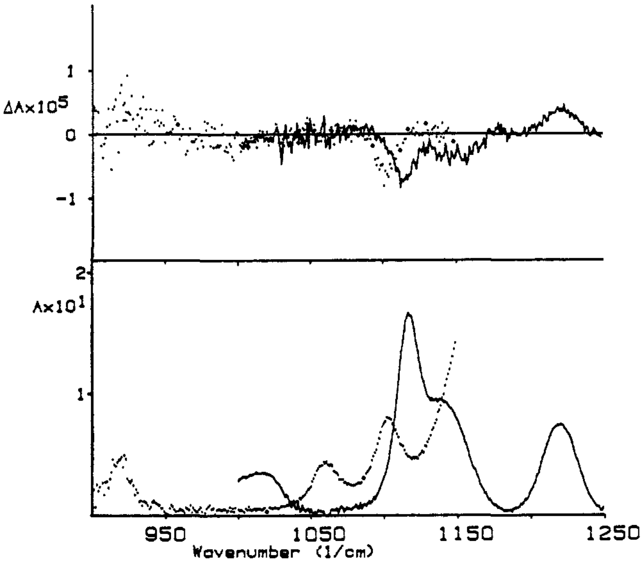

Figure 3. Infrared (bottom) and infrared VCD (top) spectra of L-Ala (solid) and L-Ala-N-d_3 (dotted), 900–1250 cm^{-1}: concentration, 1.75 M; path length 15 μm; time constant, 1 s; band-pass 5 cm^{-1}; 10 scans averaged; no smoothing.

mation modes. The assignment[10] of these bands is summarized in Table I. The IR and VCD data, both obtained as 1.2 M solutions, are not scaled; thus, the near identical intensities for the peaks at 1381, 1417, and 1470 cm^{-1} indicate the similarity of these vibrations between L-Ala and L-Ala-N-d_3.

Therefore, the intensity and frequency changes observed in the methine deformations (1358 and 1306 cm^{-1}) upon N-deuteriation (to 1343 and 1295 cm^{-1}) is quite surprising, particularly since these vibrations are a group frequency in many chiral species containing a single methine hydrogen. Thus, the data presented here indicate some vibrational coupling of the methine C–H deformation with either N–H deformation or the C–N stretching mode.

In the deuteriated species, the observed VCD is a conservative couplet within the accuracy of the instrument, with all the observed intensities located under the two methine deformations. In the undeuteriated species, the total VCD intensity in the 1250–1450 cm^{-1} region is nearly conservative as well (i.e., the integrated intensity is close to zero); however, there is considerably more negative intensity in the band at 1358 cm^{-1}, and some positive intensity at 1418 cm^{-1}, which is associated with the symmetric stretching mode of the $-CO_2^-$ group.

The conclusion, in terms of the vibrational motions involved, one may draw from these observation is that the methine deformations are somewhat coupled to the vibrations of the $-NH_3^+$ group, such that their vibrations are influenced by deuteriation at the nitrogen. Coupling with the $-CH_3$ group appears to be less, since the Raman spectra of L-Ala-C-d_3 show little change in the methine vibrational frequencies.[10] In addition, there seems to be some coupling between the methine C–H deformation and the carboxylic anion symmetric stretching mode, which is lessened by N-deuteriation, as indicated by the changes in VCD intensities between L-Ala and L-Ala-N-d_3.

Although these interactions between vibrations on different groups may be useful to interpret small changes in the VCD spectra between the isotopic species, they give no clue on the origin of the large VCD intensities observed. From simple qualitative theoretical considerations, the positive/negative intensity pattern in the methine C–H deformations (which result via a chiral perturbation from a degenerate deformation) may be expected. However, the simplest VCD intensity model, the fixed partial charge (FPC) method, fails to produce even approximate signal magnitudes;[6a] worse yet, due to the difficulties in describing the exact direction of the methine C–H deformations in terms of generalized valence or Urey–Bradley force constants, the sign patterns calculated may not even be reliable.

Thus, from a computational/theoretical viewpoint, ab initio calculations of the vibrational force field and atomic polar tensors (ATP) for infrared and VCD intensity calculations may be the only practical solution. Such computations have been carried out by Stephens and co-workers[11] on smaller model systems; and their practicality for molecules the size of alanine needs to be seen.

In terms of empirical models, such as the ring current model, the present results cannot be explained easily either. The ring current (RC) model, as proposed originally, postulates the creation of a cyclic electronic motion in a ring by the dilution of the electron density by a stretching mode. In the original example of RC, the methine C–H stretching mode in alanine produces a reduced electron density,[7a] which, in turn, causes electron density from the nearest heteroatom in the ring to flow toward the chiral carbon atom, setting in motion what was termed the ring current. Although this model was successful in explaining many large stretching VCD signals in various molecules, the methine deformations do not change the electron density along the C–H bond in a similar, intuitively acceptable manner as do the stretching modes. This point sheds some doubts on the overall validity of the RC model, since we believe that the only strong signals in this molecule, which are all due to different vibrations located within the same methine group, should be easily interpreted by the same model. Thus, it appears that there is a poorly understood effect which gives rise to enormously enhanced VCD intensities in the methine deformation and stretching modes.

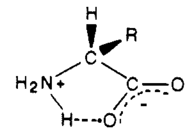

Figure 3 shows the accessible low-frequency infrared and VCD spectra of L-Ala in H_2O and L-Ala-N-d_3 in D_2O. In the former, four bands are observed at 1001, 1117, 1139, and 1221 cm^{-1}. These bands are weak in the infrared spectra. The data reported here were obtained from saturated solutions, yet, the infrared intensities at 15 μm path length are less than 0.2 absorbance unit. Use of a longer path length is not possible due to high solvent absorption.

These four bands had been assigned previously on the basis of solution-phase Raman[10] data of five isotopically labeled analogues. The broad peak at 1221 and the broad shoulder at 1139 cm^{-1}, which disappear upon deuteriation, were assigned to the two $-NH_3^+$ rocking modes. They exhibit small, but observable, VCD. Because of their low absorption intensities, the anisotropies of the vibrations in the 900–1250 cm^{-1} region are actually relatively large.

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The magnitude of the IR and VCD intensities for these vibrations is about that calculated earlier via the fixed partial charge (FPC) formalism, whereas the signals in the methine deformations are much more intense than those calculated via the FPC approach.

For the above-mentioned $-NH_3^+$ rocking modes, $\Delta A/A$ of about 5×10^{-5}, and opposite sign, as expected from qualitative group theoretical considerations, was observed. The sharp peak at 1117 cm^{-1}, which exhibits $\Delta A/A$ of -4.7×10^{-5}, was previously[12] assigned to the "antisymmetric" C–C–N stretching mode (the response of the C–C and C–N stretching modes to deuteriation of the amine and the methyl function has suggested that these stretches are more adequately described in terms of a "symmetric" and an "antisymmetric" C–C–N stretching motion).[12]

On the basis of solid-phase Raman work, the peak at 1001 cm^{-1} actually contains two accidentally degenerate vibrations, the $C^*–C_C$ stretching and a methyl rocking vibration.[10] Here, C_C denotes the carbon atom of the carboxylate group. This vibration does not exhibit any VCD intensity.

The low-frequency (900–1150 cm^{-1}) region of L-Ala-N-d_3 contains, according to the vibrational assignment published earlier, two methyl rocking modes (1060 and 918 cm^{-1}), the $C^*–C_C$ (1103 cm^{-1}) and the C–C–N "antisymmetric" stretching modes. All these vibrations are strongly perturbed, as compared to the parent molecule. Among these vibrations, the $C^*–C_C$ stretching vibration exhibits a clearly observable VCD signal, whereas the low-frequency $-CH_3$ rocking band at 920 cm^{-1} exhibits barely observable VCD ($S/N \approx 2$). This is, partially, due to the transmission cutoff of some optical elements[8] in the Hunter College VCD instrument, which can be eliminated relatively easily, opening the possibility of extending the range accessible to VCD measurements in aqueous solutions to about 800 cm^{-1}. The cuttoff in the spectra of L-Ala in H_2O, on the other hand, is due to water itself, and therefore, spectra probably cannot be extended further toward lower wavenumber.

The limitations of the solvents may explain why there is, at present, no apparent correlation between the L-Ala and the L-Ala-N-d_3 VCD spectra in the low-frequency region. This is particularly obvious when one tries to follow the vibrations upon isotopic substitution. The $-NH_3^+$ rocking modes, which show distinct VCD in L-Ala, cannot be observed in L-Ala-N-d_3, since they occur below 850 cm^{-1}. Similarily, the CCN "antisymmetric" stretching mode, which is observable in L-Ala, shifts to higher frequency in L-Ala-N-d_3 (1148 cm^{-1}) and is partially obscured by the D_2O deformation. Finally, the two modes that show VCD in L-Ala-N-d_3 have their corresponding vibrational frequencies in L-Ala just at the water cutoff at 1000 cm^{-1}.

Nevertheless, the ability to observe $-CH_3$ and $-NH_3^+$ rocking VCD from these aqueous solutions, as well as some of the skeletal stretching VCD, will open the possibilities to utilize these vibrations for purposes of vibrational assignments and conformational analyses.

Conclusions

The feasibility of observing VCD in aqueous solutions in the midinfrared region has been demonstrated. Aside from very intense methine deformation vibrations, VCD signal can be observed in rocking modes as well as skeletal stretching vibrations.

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Vibrational Circular Dichroism in the Methine Bending Modes of Amino Acids and Dipeptides

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Abstract: The vibrational circular dichroism (VCD) spectra of several amino acids and dipeptides in aqueous solution in the methine bending region (1200–1400 cm^{-1}) are reported. In both H_2O and D_2O solution, a characteristic (–,+) VCD pattern (negative at higher frequency) is observed for the two orthogonal methine bending modes in L-amino acids and L-amino acid residues only for a methine bond adjacent to a CO_2^- group. At low pH or for the N-terminus of a dipeptide, no VCD intensity is observed for these modes. The "amide III" NH bending motion does not contribute to the VCD in the dipeptides since deuteration of the nitrogen leaves the overall VCD pattern unchanged. An interpretation of the signs of the VCD features using the ring current mechanism is provided.

Vibrational circular dichroism (VCD)[1–4] studies of amino acids and simple peptides in aqueous solution provide information on absolute configuration, solution conformation, and intramolecular association. Previous investigations have focused primarily on the CH stretching region.[5–8] The large positive VCD intensity bias observed in this region for the L-enantiomers at neutral or high pH has been attributed to the stretching mode of a methine bond adjacent to a CO_2^- group.[7,8] The positive VCD intensity is not observed for amino acids at low pH[1,9] for the N-terminus of a

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