# Theoretical Study of the Electronic Spectroscopy of Peptides. 2. Glycine and *N*-Acetylglycine

**Luis Serrano-Andrés* and Markus P. Fülscher**

*Contribution from the Department of Theoretical Chemistry, Chemical Centre, University of Lund, P.O.B. 124, S-221 00 Lund, Sweden*

*Received June 13, 1996. Revised Manuscript Received October 1, 1996*[⊗]

**Abstract:** The Complete Active Space (CAS) SCF method and multiconfigurational second-order perturbation theory (CASPT2) have been used in a theoretical analysis of the electronic spectra of glycine and *N*-acetylglycine. The calculations comprise a large number of singlet valence and Rydberg excited states. The electronic spectrum of glycine is dominated by excitations located at the carboxylic acid group. Two valence $\pi \rightarrow \pi^*$ states (named $NV_1'$ and $NV_2'$) have been computed at 8.10 and 10.20 eV with intensities 0.194 and 0.125, respectively. We found in glycine two weak valence $n \rightarrow \pi^*$ states 5.65 and 6.51 eV above the ground state. One involves excitations from the lone pair orbital on the carboxylic oxygen. The second can be characterized as an intramolecular charge transfer state from the amine terminal group to the peptide unit. A $n \rightarrow \sigma^*$ excited state comprising excitations from the in-plane lone pair of the nitrogen is suggested to be responsible for a weak band around 8.6 eV. The spectrum of *N*-acetylglycine is shown to be composed of the superposition of the spectra of the peptide bond and the carboxylic acid group, the chromophores forming the system. We computed for *N*-acetylglycine the $NV_1$ amide band at 6.76 eV, the $NV_1'$ acid band at 8.55 eV, the $NV_2$ band at 9.51 eV, and an intramolecular charge transfer state at 10.13 eV as the most intense features of the absorption spectrum. Based on these results and qualitative calculations on a simple dipeptidic system the most important features of the spectra of larger polypeptides are suggested to be composed of the following excitations: a weak band at 5.5 eV is caused by the $n \rightarrow \pi^*$ excitation from the oxygen lone pairs, a band at 6.5 eV due to $\pi \rightarrow \pi^*$ $NV_1$ transitions localized at the peptide group, a band at 7.5 eV due to charge transfer states involving electronic transitions between neighboring peptide units, and a broad band at higher energies which is mainly composed of the second $\pi \rightarrow \pi^*$ $NV_2$ valence state of the peptide group.

## 1. Introduction

Electronic spectra of proteins can be considered as a superposition of spectra of individual components that make up the molecules and can be attributed to three groups of chromophores: aromatic side chains, the peptide bond, and terminal amino and carboxyl groups. Such complex spectra cannot be understood unless the spectra of the individual components are properly assigned. Earlier, we have presented calculations on the aromatic amino acids tryptophan, phenylalanine, and tyrosine, and, in addition, histidine. In these studies the chromophores were modeled by benzene, phenol, indole, and imidazole, respectively.[1−4] Recently, we presented a paper on the spectroscopic properties of the amide group as modeled by formamide and some of its alkylated derivatives.[5] In this paper we report on the absorption spectrum of glycine and *N*-acteylglycine. These molecules have been selected as models for the contribution of terminal amino and carboxyl groups to the electronic spectrum of proteins, and to bear new insight in the origin of the 7.5-eV band observed in proteins.[6]

To predict electronic spectra from first principles is a difficult task. Qualitative and quantitative correct results can only be obtained if all valence electrons are included in the treatment of electron correlation. The calculations presented here proceed in two steps: First, multiconfigurational wave functions are determined for all states of interest using the complete active space (CAS) SCF method. In the second step, the CASSCF wave function is used as a reference function for the treatment of remaining correlation effects by second-order perturbation theory, the so-called CASPT2 method. The CASSCF/CASPT2 approach has been applied to a large number of different molecular systems.[2,7] The results are consistently of high accuracy; excitation energies are reproduced with an accuracy of 0.2 eV and better where comparison with experiment in the gas phase can be made.

Gas-phase spectra of the simple amides have been interpreted as five-band systems including transitions named W, $R_1$, $NV_1$, $R_2$, and Q according to Mulliken's nomenclature. In 1953 Hunt and Simpson[8] reported ultraviolet spectra for some simple amides. Originally, these authors assumed that the two valence $\pi \rightarrow \pi^*$ bands in formamide, named $NV_1$ and $NV_2$, were placed around 7.2 and 9.2 eV, respectively. However, Hunt and Simpson also studied *N*,*N*-dimethylformamide which has a new band at about 7.7 eV. To explain its origin Hunt and Simpson assumed that the second $\pi \rightarrow \pi^*$ transition has shifted as much as 1.5 eV to lower energies upon alkyl substitution. Four years later Peterson and Simpson[9] reported the electronic spectrum of myristamide in the crystalline phase. In accord with previous

[⊗] Abstract published in *Advance ACS Abstracts,* November 1, 1996.

(1) Roos, B. O.; Fülscher, M. P.; Malmqvist, P.-Å.; Merchán, M.; Serrano-Andrés, L. In *Quantum Mechanical Electronic Structure Calculations with Chemical Accuracy*; Langhoff, S. R., Ed.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1995; p 357.

(2) Roos, B. O.; Andersson, K. *Chem. Phys. Lett.* **1995**, *245*, 215.

(3) Serrano-Andrés, L.; Roos, B. O. *J. Am. Chem. Soc.* **1996**, *118*, 185.

(4) Serrano-Andrés, L.; Fülscher, M.; Roos, B. O.; Merchán, M. *J. Phys. Chem.* **1996**, *100*, 6484.

(5) Serrano-Andrés, L.; Fülscher, M. P. *J. Am. Chem. Soc.* **1996**, *118*, 12190.

(6) Robin, M. B. *Higher Excited States of Polyatomic Molecules*; Academic Press: New York, 1975; Vol. II.

(7) Roos, B. O.; Andersson, K.; Fülscher, M. P.; Malmqvist, P.-Å.; Serrano-Andrés, L.; Pierloot, K.; Merchán, M. In *Advances in Chemical Physics: New Methods in Computational Quantum Mechanics*; Prigogine, I., Rice, S. A., Eds.; John Wiley & Sons: New York, 1996; *Vol. XCIII*, p 219.

(8) Hunt, H. D.; Simpson, W. T. *J. Am. Chem. Soc.* **1953**, *75*, 4540.

(9) Peterson, D. L.; Simpson, W. T. *J. Am. Chem. Soc.* **1957**, *79*, 2375.

S0002-7863(96)01997-X CCC: $12.00 

work they considered the 6.7- and 7.7-eV bands to be due to $\pi \rightarrow \pi^*$ excited valence states, although the 7.7-eV band was never observed in a crystalline environment.

Carboxylic acids are expected to have similar electronic spectra as the analogous amides since the $\pi$-systems are isoelectronic. Therefore, the electronic spectra of simple carboxylic acids, such as formic or acetic acid, as well as the corresponding esters, have been interpreted within the same band scheme as the amides (W′, $R_1$′, $NV_1$′, $R_2$′, and Q′ bands).[6] Primed symbols are therefore employed to name transitions originating from the carboxylic acid fragment. In 1973 McMillin *et al*.[10] measured electronic spectra of several monomeric amino acids and derivative polymers. They observed a band at 7.5 eV which, in accord with Peterson and Simpson, was assigned to a $\pi \rightarrow \pi^*$ transition.

The assignment of Hunt and Simpson, in particular the origin of the band placed at about 7.5 eV, has been questioned for quite some time.[6] However, it has been only recently that Clark[11] published a detailed crystal spectra of *N*-acetylglycine which allows the identification of the bands conclusively. In agreement with our previous calculations,[5] Clark observed two $\pi \rightarrow \pi^*$ valence transitions related to the amide group, one (called $NV_1$) placed at about 6.5 eV, and a second ($NV_2$) above 9.0 eV. The former carries most of the intensity and was shown to be proportional to the number of peptide units in proteins. In the gas phase, Clark also observed an additional weak $n \rightarrow \pi^*$ band (W band) placed at about 5.5 eV as well as a number of Rydberg transitions. In the high-energy tail of the intense $\pi \rightarrow \pi^*$ transition several weak features can be seen. They have been attributed to Rydberg 3p and 3d states as well as $n \rightarrow \sigma^*$ transitions.[6] In addition to the transitions related to the amide group, Clark[11] identified two transitions thought to be related to the carboxylic acid group: one short-axis polarized band near 8.0 eV ($NV_1$′ band) and one weak shoulder at 6.9 eV ($R_1$′ band).

The present calculations support Clark's assignments in *N*-acetylglycine and show that the 6.5-eV band in polypeptides is related to the $NV_1$ band within the peptide bond. The next intense excited valence state ($NV_1$′) was calculated 8.55 eV above the ground state and corresponds to the $\pi \rightarrow \pi^*$ transition localized on the carboxylic acid. In the energy range between 6.5 and 8.5 eV we found a number of Rydberg and $n \rightarrow \pi^*$ excited states all being characterized by small oscillator strengths. Among these, we also located a charge transfer state which is associated with the migration of an electron from the carboxylic acid to the $\pi^*$ orbital located at the peptide bond.

From the present and earlier results for these model systems we cannot find any suitable state which may correspond to the origin of the 7.5-eV band in proteins. However, the presence of a large number of peptide units in a polypeptide allows for a large number of charge transfer transitions among the subunits. The presence of a weak charge transfer band in glycine close to 7.0 eV suggests these transitions might not be at high energies and therefore the 7.5-eV band could be due to charge transfer states involving neighboring peptide units. To test this hypothesis we also computed the electronic spectrum of a model dipeptide. At a qualitative level these calculations indicate the presence of such charge transfer states at energies close to 7.5 eV with a computed intensity about a third of that of the $NV_1$ band.

(10) McMillin, C. R.; Rippon, W. B.; Walton, A. G. *Biopolymers* **1973**, *12*, 589.
(11) Clark, L. B. *J. Am. Chem. Soc.* **1995**, *117*, 7974.

## 2. Methods and Computational Details

Experiments[12] and earlier theoretical studies[13,14] established that glycine assumes a planar conformation in the gas phase. Similarly, acetylglycine has been shown to be almost planar in the crystal phase.[11] For reasons of consistency, the ground-state geometries of the present molecules were thus optimized at the MP2 level using the 6-31G* basis sets and imposing constraints to maintain $C_s$ symmetry.

The calculation of excited states requires basis sets of high quality. We used atomic natural orbital (ANO) type basis sets[15] of triple-$\zeta$ plus polarization quality for the first-row atoms (C,N,O 4s3p1d/H 2s). These basis sets were supplemented with a 1s1p1d set of Rydberg-type functions. The latter were determined separately for each molecule following the procedure described earlier[1] and placed at the average charge centroid of the $^2$A′ and $^2$A″ cations. Exponents and coefficients for the diffuse functions are given in Supporting Information. The 1s electrons of the first-row atoms were kept frozen in the form determined by the ground-state SCF wave function and were not included in the calculation of the correlation energy.

The CASSCF/CASPT2 method[2,16−18] was used for all excited-state calculations. This method is a two-step procedure to calculate state energies corrected through second order in perturbation theory with a CASSCF wave function constituting the reference function. In general, the active space is chosen such as to include all strongly correlating orbitals, i.e., orbitals with occupation numbers appreciably different from 2 or 0. Thereby all static correlation and near-degeneracy effects are included in the CASSCF reference function, and consequently there will be no large terms in the perturbation expansion. Recently, a level shift technique has been introduced,[2,19] the socalled LS-CASPT2 approach, which allows the effect of intruder states common in many calculations on excited states to be avoided. Here, a value of 0.3 au has been used for the level shift in all the computed states. Finally, transition properties were obtained by combining the CASSCF transition moments—calculated with the CAS State Interaction (CASSI)[20] method—with excitation energies evaluated using the CASPT2 energies.

For the present molecules the active spaces were chosen as follows: (a) glycine—in $C_s$ symmetry, the three $\pi$ orbitals located on the carboxylic acid group and the two $\sigma$ lone pair orbitals located at the carboxylic oxygen and nitrogen span the minimal active space labeled (2,3), which is the number of a′ and a″ orbitals, respectively, and the number of active electrons is six; (b) *N*-acetylglycine—since *N*-acetylglycine may be considered as a covalently linked acid and amide group, the minimal active space is given by the sum of the minimal active spaces needed to properly describe these subunits. It consists of six $\pi$-orbitals and two $\sigma$ lone-pair orbitals located at the carboxylic oxygens, including 12 electrons, and is labeled (2,6).

In numerous calculations we have shown[1] that Rydberg states may interact with valence states and may lead to erratic results. The recommended procedure is therefore to always include diffuse functions in the basis set and Rydberg-type orbitals in the active space. Thus, to compute the lowest (3s, 3p, and 3d) Rydberg series we should include nine additional orbitals, six of a′ symmetry and three of a″ symmetry. This leads, however, to active spaces exceeding the limits of our present implementation of the CASSCF program. Therefore, we proceeded in two steps and first considered only the 3s and 3p Rydberg orbitals. Three a′ orbitals and one a″ orbital were added to the valence active space. All calculations needed to characterize the 3s and 3p Rydberg

(12) Iijima, K.; Tanaka, K.; Onuma, S. *J. Mol. Struct.* **1991**, *246*, 257.
(13) Császár, A. G. *J. Am. Chem. Soc.* **1992**, *114*, 9568.
(14) Hu, C.-H.; Shen, M.; Schaefer, H. F. S., III *J. Am. Chem. Soc.* **1993**, *115*, 2923.
(15) Widmark, P.-O.; Malmqvist, P.-Å.; Roos, B. O. *Theor. Chim. Acta* **1990**, *77*, 291.
(16) Roos, B. O. In *Advances in Chemical Physics*; *Ab Initio Methods in Quantum Chemistry*; Lawley, K. P., Ed.; John Wiley & Sons Ltd.: Chichester, England, 1987; Vol. II, Chapter 69, p 399.
(17) Andersson, K.; Malmqvist, P.-Å.; Roos, B. O.; Sadlej, A. J.; Wolinski, K. *J. Phys. Chem.* **1990**, *94*, 5483.
(18) Andersson, K.; Malmqvist, P.-Å.; Roos, B. O. *J. Chem. Phys.* **1992**, *96*, 1218.
(19) Roos, B. O.; Andersson, K.; Fülscher, M. P.; Serrano-Andrés, L.; Pierloot, K.; Merchán, M.; Molina, V. *J. Mol. Struct. (Theochem)* **1996**, in press.
(20) Malmqvist, P. Å.; Roos, B. O. *Chem. Phys. Lett.* **1989**, *155*, 189.

**Table 1.** Calculated and Experimental Excitation Energies (eV), Oscillator Strengths, Dipole Moments $\mu$ (D), Spatial Extension $\langle r^2 \rangle$ (au), and Transition Moment Directions (deg) for the Excited Singlet States in Glycine

| | | excitation energies | | | | oscil str | TM dir[b] |
|---|---|---|---|---|---|---|---|
| state | symbol[a] | PT2 | exp[c] | $\mu$ | $\langle r^2 \rangle$ | tw[a] | tw[a] |
| $1^1A'$(G.S.) | | | | 1.24 | 69 | | |
| $1^1A''(n_O \rightarrow \pi^*)$ | W′ | 5.65 | 5.8−6.0 | 2.15 | 65 | 0.001 | |
| $2^1A'(n_N \rightarrow 3s)$ | | 6.09 | | 2.72 | 107 | 0.005 | −30 |
| $2^1A''(n_N \rightarrow \pi^*)$ | | 6.51 | | 9.25 | 60 | 0.003 | |
| $3^1A'(n_O \rightarrow 3s)$ | $R_1'$ | 6.98 | 6.9−7.0 | 4.20 | 126 | 0.059 | +41 |
| $3^1A''(n_N \rightarrow 3p_z)$ | | 6.99 | | 0.90 | 136 | 0.0001 | |
| $4^1A'(n_N \rightarrow 3p_y)$ | | 7.19 | | 3.25 | 141 | 0.003 | −71 |
| $5^1A'(n_N \rightarrow 3p_x)$ | | 7.57 | | 9.50 | 132 | 0.013 | +74 |
| $6^1A'(n_O \rightarrow 3p_x)$ | | 7.67 | | 5.78 | 122 | 0.004 | +89 |
| $7^1A'(n_N \rightarrow 3d_{x^2-y^2})$ | | 7.77 | | 8.85 | 209 | 0.006 | +90 |
| $4^1A''(\pi_2 \rightarrow 3s)$ | | 7.90 | | 5.29 | 104 | 0.00001 | |
| $5^1A''(n_O \rightarrow 3p_z)$ | | 7.99 | | 5.51 | 163 | 0.002 | |
| $8^1A'(n_O \rightarrow 3p_y)$ | | 8.01 | | 3.61 | 145 | 0.007 | +87 |
| $9^1A'(n_O \rightarrow 3d_{z^2})$ | | 8.02 | | 10.00 | 214 | 0.003 | −71 |
| $10^1A'(n_O \rightarrow 3d_{xy})$ | | 8.09 | | 11.98 | 213 | 0.069 | +41 |
| $11^1A'(\pi \rightarrow \pi^*)$ | $NV_1'$ | 8.10 | 8.0−8.2 | 3.26 | 71 | 0.194 | −55 |
| $6^1A''(n_N \rightarrow 3d_{xz})$ | | 8.11 | | 9.80 | 175 | 0.001 | |
| $7^1A''(n_N \rightarrow 3d_{yz})$ | | 8.19 | | 9.96 | 208 | 0.001 | |
| $12^1A'(n_N \rightarrow 3d_{xy})$ | | 8.43 | | 14.31 | 211 | 0.014 | +74 |
| $13^1A'(n_O \rightarrow 3d_{x^2-y^2})$ | | 8.59 | | 6.75 | 211 | 0.005 | +89 |
| $14^1A'(n_N \rightarrow 3d_{z^2})$ | | 8.60 | | 10.87 | 213 | 0.007 | +87 |
| $15^1A'(n_N \rightarrow \sigma^*)$ | | 8.86 | 8.5 | 5.37 | 102 | 0.047 | −88 |
| $16^1A'(\pi_2 \rightarrow 3p_z)$ | $R_2'$ | 8.99 | 8.9 | 0.44 | 138 | 0.031 | −44 |
| $8^1A''(n_O \rightarrow 3d_{yz})$ | | 9.02 | | 8.45 | 209 | 0.0001 | |
| $9^1A''(n_O \rightarrow 3d_{xz})$ | | 9.13 | | 5.32 | 208 | 0.004 | |
| $10^1A''(\pi_2 \rightarrow 3p_x)$ | | 9.17 | | 2.87 | 130 | 0.019 | |
| $11^1A''(\pi_2 \rightarrow 3p_y)$ | | 9.53 | | 3.25 | 152 | 0.014 | |
| $17^1A'(\pi_2 \rightarrow 3d_{xz})$ | | 9.91 | | 2.98 | 214 | 0.035 | −44 |
| $18^1A'(\pi_2 \rightarrow 3d_{yz})$ | | 10.20 | | 1.69 | 210 | 0.005 | +9 |
| $19^1A'(\pi \rightarrow \pi^*)$ | $NV_2'$ | 10.21 | 10.0 | 3.41 | 87 | 0.125 | +18 |
| $20^1A'(n_O \rightarrow \sigma^*)$ | | 10.22 | | 3.61 | 101 | 0.086 | −41 |
| $12^1A''(\pi_2 \rightarrow 3d_{xy})$ | | 10.26 | | 2.84 | 215 | 0.0001 | |
| $13^1A''(\pi_2 \rightarrow 3d_{x^2-y^2})$ | | 10.30 | | 8.65 | 213 | 0.00001 | |
| $14^1A''(\pi_2 \rightarrow 3d_z^2)$ | | 10.32 | | 1.37 | 214 | 0.0001 | |

[a] See text. tw: This work. [b] The molecule is placed in the *xy* plane ($C_s$ symmetry). The used convention places the *y* axis along the CO bond and the oxygen in the fourth quadrant. The positive angles are defined clockwise from the *y* axis in the first quadrant as in ref 11. See Figure 1. [c] See text for the discussion of the experimental values.

states are carried out, and, finally, the 3s and 3p Rydberg orbitals are removed from the orbital space. In successive steps the 3d Rydberg orbitals take their place and the process is reiterated. Finally, the valence state properties are determined from CASSCF wave functions where all Rydberg orbitals were removed from the active space. This procedure has been used and carefully tested in several earlier applications.[1−3,21] Finally, one additional $\sigma$ orbital was finally included in the active space of both systems in order to search for possible $\sigma \rightarrow \sigma^*$ and $\pi \rightarrow \sigma^*$ transitions.

The calculations have been performed with the MOLCAS-3[22] program package on IBM RS/6000 workstations except for the MP2 optimizations which used the MULLIKEN[23] program.

## 3. Results and Discussion

**1. Glycine.** Spectra of aliphatic amino acids in solution have been presented,[24] but a complete interpretation of the main bands has not been provided. McMillin *et al.*[10] reported the vacuum ultraviolet spectra of a series of poly(α-amino acid)s. Films of the amino acids were obtained by casting samples onto lithium fluoride crystals and evaporating the solvent at room temperature. In another experiment vacuum sublimation was used by Inagaki[25] to record far ultraviolet (down to 115 nm) absorption spectra of aliphatic amino acids. Vinogradov and Dodonova[26] have also measured the spectra of a number of solid films of aliphatic amino acids. Furthermore, Snyder *et al.*[27] studied circular dichroism in solutions of some amino acids. To interpret these spectra, Inagaki[25] applied the classical four-band model which has been derived for amides.[28] This model is based on semiempirical calculations that were refined by Clark.[11] To our knowledge these are the only calculations which have been performed for the electronic spectra of amino acids.

Table 1 compiles the results for the computed absorption spectrum of the glycine molecule. The table includes excitation energies, dipole moments, transition intensities, and transition moment directions. Two valence $\pi \rightarrow \pi^*$, two valence $n \rightarrow \pi^*$, and three different Rydberg series arising from the highest $\pi$ and the lone-pair $n_O$ and $n_N$ orbitals have been included in the calculations of the glycine molecule. In addition, two $\sigma \rightarrow \sigma^*$ states also have been computed.

(21) Fülscher, M. P.; Roos, B. O. *J. Am. Chem. Soc.* **1995**, *117*, 2089.
(22) Andersson, K.; Fülscher, M. P.; Karlström, G.; Lindh, R.; Malmqvist, P.-Å.; Olsen, J.; Roos, B. O.; Sadlej, A. J.; Blomberg, M. R. A.; Siegbahn, P. E. M.; Kellö, V.; Noga, J.; Urban, M.; Widmark, P.-O. *MOLCAS Version 3*; Department of Theoretical Chemistry, Chemistry Center, University of Lund, P.O.B. 124, S-221 00 Lund, Sweden, 1994.
(23) Rice, J. E.; Horn, H.; Lengsfield, B. H.; McLean, A. D.; Carter, J. T.; Replogle, E. S.; Barnes, L. A.; Maluendes, S. A.; Lie, G. C.; Gutowski, M.; Rudge, W. E.; Sauer, S. P. A.; Lindh, R.; Andersson, K.; Chevalier, T. S.; Widmark, P.-O.; Bouzida, D.; Pacanski, G.; Singh, K.; Gillan, C. J.; Carnevali, P.; Swope, W. C.; Liu, B. *MULLIKEN Version 1.1.0*; Almaden Research Center, IBM Research Division, 6500 Harry Road, San Jose, CA, 95120-6099, 1994.
(24) Wetlaufer, D. B. Ultraviolet spectra of proteins and amino acids. In *Advances in Protein Chemistry*; Anfinsen, C. B.; Anson, M. L.; Bailey, K.; Edsall, J. T., Eds.; Academic Press: New York, 1962; Vol. 17.
(25) Inagaki, T. *Biopolymers* **1973**, *12*, 1353.
(26) Vinogradov, I. P.; Dodonova, N. Y. *Opt. Spectrosc.* **1971**, *30*, 14.
(27) Snyder, P. A.; Vipond, P. M.; Johnson, W. C. *Biopolymers* **1973**, *12*, 975.
(28) Basch, H.; Robin, M. B.; Kuebler, N. A. *J. Chem. Phys.* **1968**, *49*, 5007.

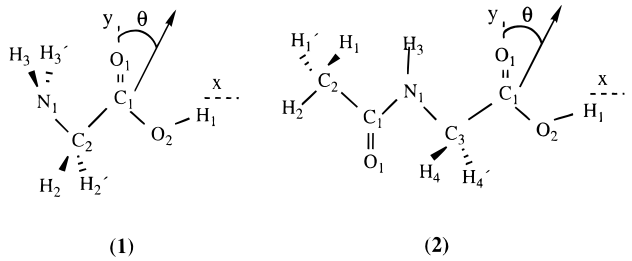
A weak band has been described around 6.0 eV in different solvents and solid media[6,10,25] and it was suggested that it is related to the $n_O \rightarrow \pi^*$ band found in the gas-phase spectra of formic and acetic acid around 5.8 eV. This band was given the name W′ [11] to distinguish it from the W band (also $n_O \rightarrow \pi^*$) in amides. We computed an excitation energy of 5.65 eV and oscillator strength of 0.001 for this transition. Moreover, the structure of the wave function indicates that it corresponds to the weak transition found in amides around 5.5 eV.[5] We cannot rule out some contribution to the intensity from the transition to the $2^1A'(n_N \rightarrow 3s)$ state, computed at 6.09 eV with an intensity of 0.005. This is a Rydberg transition and is expected to vanish in condensed phases. However, there is a strong evidence that the Rydberg transitions do not disappear completely. Clark[11] finds in the crystal spectrum of *N*-acetylglycine a weak in-plane polarized absorption which cannot correspond to the $n \rightarrow \pi^*$ transitions.

McMillin *et al.*[10] and Inagaki[25] found a second band with medium intensity at energies close to 6.9 eV. However, the presence of the band even in condensed phases led Inagaki[25] to disclaim its assignment as a Rydberg transition. A similar band was found at 7.1 eV in the gas-phase spectrum of the acetic acid.[6,29] We computed the transition to the $3^1A'(n_O \rightarrow 3s)$ state at 6.98 eV with an intensity of 0.059. Similar to the situation found in amides,[5] this band has unstructured character. We agree with Clark[11] that the assignment of the band is the $n_O \rightarrow 3s$ Rydberg transition, in spite of the fact that it is visible in condensed phases. In the absorption spectra of glycine reported by Inagaki[25] this band appears as a shoulder of the most intense band. In larger amino acids the most prominent feature displaces to lower energies and the $n_O \rightarrow 3s$ is overlapped. McMillin *et al.*[10] interpret the band as the first $\pi \rightarrow \pi^*$ valence state in glycine but this possibility was completely ruled out by our calculations.

We computed the most intense band at 8.10 eV with an oscillator strength of 0.194. The wave function is characteristic for a $\pi \rightarrow \pi^*$ promotion to the $NV_1'$ valence state. The band was reported at 7.9 eV in solid films[25] of glycine and at 7.95 eV for acetylglycine in Clark's[11] crystal spectrum. The transition moment polarization measured by Clark offers two alternative directions in acetylglycine of $4 \pm 3°$ and $-61 \pm 3°$. The latter is in agreement with our computed result of $-55°$ in glycine. The $NV_1'$ band is also found in carboxylic acids at energies ranging from 7.8 to 8.3 eV.[6,29] The band is known to decrease in energy in larger amino acids and has been observed in solid phases at 7.4, 7.1, and 7.0 eV for alanine, valine, and leucine, respectively.[25]

A fourth, prominent band has been described in the solid-state spectrum of glycine around 8.6 eV.[25] However, the strong background absorption makes the results somewhat uncertain. On the other hand, the intensity of this band strongly increases for larger amino acids and thus seems to assure the presence of the band also in glycine with less than a fourth of the intensity of the $NV_1'$ band. The nature of this band is uncertain. A possible assignment to the $R_2'$ Rydberg band, proposed by Basch *et al.*,[28] is unlikely. Robin[6] suggested, on the basis of the observed intensity, that it was the $n_O \rightarrow \sigma^*$ transition. This band is also observed near 8.5 eV in the solid film spectra of several amino acids in their zwitterionic form by Vinogradov and Dodonova.[26] The increasing intensity of this band in amino acids with larger alkyl chains such as valine or leucine[25] also suggest that the band is of valence nature.

We have computed two different $\sigma \rightarrow \sigma^*$ transitions in glycine at energies above 8.5 eV. The transition to the $14^1A'(n_N \rightarrow \sigma^*)$ state is computed at 8.86 eV in the gas phase with an intensity of 0.047, and that to the $19^1A'(n_O \rightarrow \sigma^*)$ state at 10.22 eV with an intensity of 0.086. These results suggest that the observed band at 8.5 eV is due to an in-plane transition from the in-plane lone pair of the nitrogen to an antibonding $\sigma$ orbital. To our knowledge, such a possibility has never been reported before. The $n_O \rightarrow \sigma^*$ excitation from the oxygen lone pair appears too high in energy. This result is also consistent with our calculations on simple amides in which the $n_O \rightarrow \sigma^*$ band always appeared above 10.0 eV. Furthermore, the $n \rightarrow \sigma^*$ nature of the band is also supported by the behavior of the transition in larger amino acids.[25] As the alkyl chain attached to the central carbon of the amino acid increases, the excitation energy decreases and the intensity increases. In valine the band appears at 7.9 eV and is shifted to 7.7 eV in leucine. The latter has an intensity almost as large as the $\pi \rightarrow \pi^*$ transition.[25] The band at 8.5 eV also does not correspond to the second $\pi \rightarrow \pi^*$ $NV_2'$ valence state. We predict an excitation energy of 10.21 eV for this state similar to the situation found in carboxylic acids.[6,29]




(**1**) (**2**)

**Figure 1.** Structure and atom labeling of the molecules. (**1**) glycine and (**2**) *N*-acetylglycine ($C_s$ symmetry). The arrow defines the positive angles ($\theta$) of the transition moment directions.

**2. *N*-Acetylglycine.** The absorption spectrum of *N*-acetylglycine is expected to ressemble the superimposed spectra of a simple amide and the carboxyl chromophore. Additionally, new intramolecular charge transfer bands may be observed. Recently Clark[11] reported a detailed study on the crystal spectrum of this molecule, including transition energies, intensities, and transition moment directions. In the crystal phase the molecule occurs as the neutral species. Table 2 compiles our computed results together with the most probable assignments for the experimental bands.

The model spectrum proposed by Clark for acetylglycine includes one $n \rightarrow \pi^*$ (W band), two $\pi \rightarrow \pi^*$ ($NV_1$ and $NV_2$ bands), and one Rydberg ($R_1$ band) transitions corresponding to the peptide chromophore and another set of bands with the same characteristics for the carboxylic acid group (Clark[11] uses the symbols W′, $NV_1'$, $NV_2'$, and $R_1'$ in this case). Basically the same assignments have been maintained in Table 2, although new transitions have been included. In order to compare to glycine, the same convention for the transition moment directions has been selected in both cases (see Figure 1). The carbonyl C−O bond of the carboxylic acid group is selected as the reference axis. The angle is positive in the direction from this axis toward the hydroxyl group. Clark[11] used the same convention for the transitions related to the carboxylic acid group but interchanged the C−O group to that of the amide group for the transitions related to the peptide group. We will also use the nomenclature $\pi_1$, $\pi_3$, and $\pi_6^*$ for the orbitals formally belonging to the carboxylic acid group and $\pi_2$, $\pi_4$, and $\pi_5^*$ for those formally belonging to the amide group.

The spectrum of acetylglycine in trimethyl phosphate[11] shows a weak transition at 5.6 eV with an estimated oscillator strength of 0.001 and a predominantly out-of-plane polarization. There

(29) Barnes, E. E.; Simpson, W. T. *J. Chem. Phys.* **1963**, *39*, 670.
(30) Onari, S. *J. Appl. Phys.* **1970**, *9*, 227.

**Table 2.** Calculated and Experimental Excitation Energies (eV), Oscillator Strengths, Dipole Moments $\mu$ (D), Spatial Extension $\langle r^2 \rangle$ (au), and Transition Moment Directions (deg) for the Excited Singlet States in *N*-Acetylglycine

| | | excited energies | | | | oscil str | | TM dir[b] | |
|---|---|---|---|---|---|---|---|---|---|
| state | symbol[a] | PT2 | exp[c] | $\mu$ | $\langle r^2 \rangle$ | tw[a] | exp[c] | tw[a] | exp[c] |
| $1^1A'$(G.S.) | | | | 2.60 | 107 | | | | |
| $1^1A''(n_{O_1} \rightarrow \pi^*)$ | W | 5.25 | 5.6[d] | 1.10 | 98 | 0.001 | 0.001 | | |
| $2^1A''(n_{O_2} \rightarrow \pi^*)$ | W′ | 5.63 | 5.9[e] | 4.90 | 98 | 0.001 | 0.001 | | |
| $3^1A''(\pi_4 \rightarrow 3s)$ | | 6.27 | | 1.86 | 144 | 0.001 | | | |
| $2^1A'(n_{O_1} \rightarrow 3s)$ | $R_1$ | 6.70 | 6.5[e] | 7.47 | 154 | 0.004 | 0.01 | −88 | |
| $3^1A'(\pi \rightarrow \pi^*)$ | $NV_1$ | 6.76 | 6.6 | 5.04 | 121 | 0.292 | 0.23 | +50 | +62 |
| $4^1A'(n_{O_1} \rightarrow 3p_x)$ | | 6.85 | | 8.05 | 172 | 0.023 | | +56 | |
| $5^1A'(\pi_4 \rightarrow 3p_z)$ | | 6.89 | | 5.05 | 181 | 0.019 | | −9 | |
| $6^1A'(\pi \rightarrow \pi^*)$ | CT | 7.05 | | 9.18 | 138 | 0.033 | | +25 | |
| $4^1A''(\pi_4 \rightarrow 3p_y)$ | | 7.06 | | 1.23 | 184 | 0.013 | | | |
| $7^1A'(n_{O_2} \rightarrow 3s)$ | $R_1'$ | 7.14 | 6.9 | 9.96 | 154 | 0.023 | 0.01 | +85 | (4, −55) |
| $5^1A''(n_{O_1} \rightarrow \pi^*)$ | CT | 7.15 | | 6.52 | 129 | 0.00001 | | | |
| $6^1A''(\pi_4 \rightarrow 3p_x)$ | | 7.19 | | 13.53 | 198 | 0.0001 | | | |
| $8^1A'(n_{O_2} \rightarrow 3p_y)$ | | 7.22 | | 2.33 | 162 | 0.033 | | −67 | |
| $7^1A''(n_{O_1} \rightarrow 3p_z)$ | | 7.24 | | 9.21 | 178 | 0.001 | | | |
| $9^1A'(n_{O_1} \rightarrow 3p_y)$ | | 7.25 | | 10.56 | 183 | 0.001 | | +45 | |
| $8^1A''(n_{O_2} \rightarrow 3p_z)$ | | 7.85 | | 1.85 | 159 | 0.0001 | | | |
| $10^1A'(n_{O_2} \rightarrow 3p_x)$ | | 8.32 | | 12.11 | 176 | 0.027 | | −16 | |
| $11^1A'(\pi \rightarrow \pi^*)$ | $NV_1'$ | 8.55 | 8.0 | 5.61 | 125 | 0.350 | 0.17 | −2 | (4, −61) |
| $12^1A'(n_{O_1} \rightarrow \sigma^*)$ | | 9.14 | | 9.11 | 185 | 0.018 | | +84 | |
| $9^1A''(\pi_3 \rightarrow 3s)$ | | 9.17 | | 1.94 | 143 | 0.017 | | | |
| $13^1A'(\pi \rightarrow \pi^*)$ | $NV_2$ | 9.51 | 8.9−9.3 | 2.93 | 121 | 0.125 | 0.1 | −21 | (−3, −54) |
| $14^1A'(\pi \rightarrow \pi^*)$ | CT | 10.13 | | 10.12 | 134 | 0.284 | | +76 | |

[a] See text. CT: charge transfer state. tw = this work. [b] Same criterion as in glycine (cf. Table 1). [c] Crystal spectrum of *N*-acetylglycine except when indicated. Reference 11. [d] Solution spectrum of *N*-acetylglycine in trimethyl phosphate. Reference 11. [e] Inferred, not directly observed, in the crystal spectrum of *N*-acetylglycine. Reference 11.

is no doubt that this band is the $n \rightarrow \pi^*$ transition corresponding to the excitation from the lone pair of the peptidic oxygen (W band). We have computed transitions to the $1^1A''$ ($n_{O_1} \rightarrow \pi^*$) state to occur at 5.25 eV with an oscillator strength of 0.001. This excitation can also be compared to equivalent states in amides[5] for which the $n \rightarrow \pi^*$ transition is observed at 5.5 eV in the gas phase. In solution the energy increases to 5.9 eV. In proteins the W band seems to slightly decrease in energy. In the crystal spectrum of acetylglycine[11] the band appears extremely weak around 5.8 eV. The second $n \rightarrow \pi^*$ state in acetylglycine is the $2^1A''(n_{O_2} \rightarrow \pi^*)$ state which was computed at 5.63 eV with an intensity of 0.001. It should constitute the W′ band, but it is not distinguishable owing to the presence of the amide W band at the same energy. Another $n \rightarrow \pi^*$ transition much higher in energy was also computed but it cannot be observed since it is hidden under other stronger bands.

The next important band is called the $R_1$ band, and it corresponds to the beginning of the Rydberg series. In simple amides,[5] a unresolved band of medium intensity has been observed near 6.5 eV. No evidence of this band is obtained from the crystal spectrum of propanamide. Clark[11] suggested that this band must overlap with the intense $\pi \rightarrow \pi^*$ $NV_1$ band and have a similar polarization. We computed the $2^1A'(n_{O_1} \rightarrow 3s)$ state at 6.70 eV with oscillator strength of 0.004 and transition moment direction of −88°. The latter, with similar polarization as the $\pi \rightarrow \pi^*$ band, is not observed. In contrast, the $R_1$ band can be detected in some small amides such as *N*-methylacetamide because the $R_1$ state lies almost 0.5 eV lower in energy than the $\pi \rightarrow \pi^*$ band.[5] The transition to the $4^1A'(n_{O_1} \rightarrow 3p_x)$ Rydberg state is computed at 6.85 eV. It has a calculated intensity of 0.023 and a polarization of +56°, again, close to that of the $\pi \rightarrow \pi^*$ state. Therefore it may be difficult to observe the $4^1A'(n_{O_1} \rightarrow 3p_x)$ Rydberg state.

The most intense $\pi \rightarrow \pi^*$ transition in the crystal spectrum of acetylglycine is the $NV_1$ band observed at 6.6 eV with an estimated oscillator strength of 0.23 and a transition moment direction of +62°.[11] It is due to the $\pi_4 \rightarrow \pi_5^*$ promotion of an electron and can be characterized as the $\pi \rightarrow \pi^*$ band of the peptide group, computed at 6.7−6.8 eV for a number of amides.[5] In acetylglycine we have computed this transition at 6.76 eV with an oscillator strength of 0.292 and a transition moment direction of +50°, in good agreement with the experimental data. This is undoubtedly the band located near 6.5 eV in other molecules such as polyamides, nylons, and other polypeptidic systems in general.[6] Taking as reference the carbonyl group of the amide, the experimental and computed transition moment directions are −55° and −43°, respectively, which is in agreement with the values observed in the simple amides.

In glycine the so-called $R_1'$ band, corresponding to the $n \rightarrow 3s$ Rydberg state involving the carboxylic oxygen, was computed at 6.98 eV. In acetylglycine the transition is computed at 7.14 eV with an oscillator strength of 0.023 and a transition moment direction of +85°. The band is located in the experimental spectrum around 6.9 eV with an estimated oscillator strength of 0.01 and transition moment directions +4° or −55°. Similar to the situation observed for propanamide,[5] the computed and measured transition moment directions for a Rydberg state do not agree. However, the clear presence of the $6^1A'(n_{O_2} \rightarrow 3s)$ Rydberg state in the condensed phase is remarkable and contradicts the assertion by Robin[6] that Rydberg states cannot be seen in condensed phases.

The second, most prominent band in the crystal spectrum of acetylglycine was reported around 8.0 eV with an intensity of 0.17 and has been assigned to the first $\pi \rightarrow \pi^*$ band of the carboxylic acid.[11] The $NV_1'$ band is due to the $\pi_3 \rightarrow \pi_6^*$ transition. For glycine, we computed this transition at 8.1 eV. In acetylglycine the band was computed to shift to 8.55 eV, in accord with the crystal spectrum. The computed oscillator strength, 0.35, is larger than for the $NV_1$ band in glycine. However, the $NV_1$ transition also appears slightly more intense in crystals (cf. Table 2).

The $NV_2$ state can be characterized as the $\pi_2 \rightarrow \pi_6^*$ excited state and is computed at 9.51 eV in acetylglycine with an oscillator strength of 0.125. Clark[11] reports a weak and broad feature between 8.9 and 9.3 eV which is usually known as the Q band, including both valence and Rydberg transitions. On

the one hand, we have not made any attempts to determine the state energies for the 3d Rydberg series. On the other hand, we searched for the lowest $\sigma \rightarrow \sigma^*$ excited state which is expected to have an energy close to 9 eV. The $n_{O_1} \rightarrow \pi^*$ transition was found at 9.14 eV with an oscillator strength of 0.018.

In addition to the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions located at the amide or acid group we also determined a number of charge transfer states. The lowest energy state originates from the $\pi \rightarrow \pi^*$ transition from the highest $\pi_4$ orbital of the peptide group to the antibonding $\pi_6^*$ orbital of the carboxylic acid group. It is computed at 7.05 eV with an oscillator strength of 0.033. It is the most intense transition in this region of the spectrum and, possibly, it may be related to the 6.9-eV feature which was assigned to the $R_1'$ band.[6] The second charge transfer band ($5^1A''$) was computed at 7.15 eV ($n_{O_1} \rightarrow \pi_6^*$ transition) and carries almost no intensity. The $13^1A'(\pi \rightarrow \pi^*)$ state can be characterized as the third charge transfer state. It has a large oscillator strength, 0.284, and is due to the propagation of an electron from the $\pi_2$ orbital to the antibonding $\pi_5^*$ orbital of the carboxylic acid group. The $\pi_2$ orbital belongs to the amide group, but, as already pointed out by Clark[11], this orbital is very delocalized and therefore the transition strength for $\pi_2 \rightarrow \pi_6^*$ is enhanced.

**3. The Spectra of Polypeptides.** To relate the computed excited-state properties of acetylglycine and closely related small systems to electronic spectra of proteins is a difficult task. Conformation, hydrogen bonding, and solvation are some of the effects that need to be considered. If we assume, however, that the spectrum of a polypeptide can be described as the superposition of the spectra of its subunits, then transition properties related to the peptide chromophore are expected to follow a simple additivity rule. On the other hand, transition properties related to terminal groups such as amine or the carboxylic acid should not be observed in the spectrum.

Electronic spectra of polypeptides in solution show a clear and intense band at 6.5 eV.[6] Comparing experiment with our calculated data we may assign this band, in accord with experiment, to the $NV_1$ transition (valence $\pi \rightarrow \pi^*$ excitation) within a peptide unit. Spectra of proteins show a second intense band close to 7.5 eV,[6] but it is not observed for other polyamides such as nylons.[30] Originally, it was assigned to the second valence $\pi \rightarrow \pi^*$ excited state of the amide group.[9] Such a model assumes, however, that the band undergoes a red shift of more than 1.5 eV as compared to formamide in the gas phase and appears to be unlikely. Because of that, Robin[6] suggested that the second, intense band in the spectra of proteins may be due to $n_O \rightarrow \sigma^*$ excitations. A critical inspection of the present and earlier results of CASSCF/CASPT2 calculations does not reveal any evidence for this interpretation. For acetylglycine the computed transition energies are 9.14 and 9.51 eV for the $n_O \rightarrow \sigma^*$ and the valence $\pi \rightarrow \pi^*$ $NV_2$ excited states, respectively.

Focusing on the polarization of the 6.5- and 7.5-eV bands, we computed the transition moment direction of the $NV_1$ band of acetylglycine to be $+50°$, in good agreement with experiment, $+62°$.[11] The $NV_2$ band is predicted to have a near short-axis polarization, $-21°$. Finally, the computed polarization of the $n_O \rightarrow \sigma^*$ band is approximately parallel to that of the $NV_1$ band. The transition moment directions of the 6.5- and 7.5-eV bands in poly(L-alanine)[6,31] were reported to have approximately parallel polarization. Thus, the 7.5-eV band appears more likely to be due to $n_O \rightarrow \sigma^*$ excitations. However, we find the intensity of the $n_O \rightarrow \sigma^*$ transition to be an order of magnitude smaller than that of the $NV_2$ and $NV_1$ bands. Moreover, hydrogen bonding to proximal proton donors and other solvation effects will possibly lead to a blue shift and weakening of the intensity of the $n_O \rightarrow \sigma^*$ transition.

The presence of a weak charge transfer band in glycine close to 7.0 eV suggests that the 7.5-eV band may be due to charge transfer states involving neighboring peptide units. To test this hypothesis, we performed some additional calculations on the most simple dipeptide: $CH_3-(CONH)-CH_2-(CONH)-CH_3$ (it can be considered the dimer of the acetamide molecule). The geometry was restricted to be planar and basis sets of double-$\zeta$ quality were used. Within this model, the CASSCF/CASPT2 calculation predicted two charge transfer transitions between each of the peptide units approximately 1 eV higher in energy than the two $NV_1$-type transitions. In agreement with experiment, the charge transfer bands were found to be long-axis polarized, and the oscillator strengths were approximately a third of the $\pi \rightarrow \pi^*$ $NV_1$-type transitions. Moreover, the lowest $n_O \rightarrow \sigma^*$ and $\pi \rightarrow \pi^*$ $NV_2$-type excited states were found 2.5−3.5 eV above the $NV_1$-type transitions.

The present model calculations suggest that the 7.5-eV band observed in proteins is of charge transfer character. Evidently, charge transfer excitations will be strongly dependent on the conformation of the peptide. Such behavior has been observed[10] experimentally for the 7.5-eV band. In large polypeptides the number of combinations of peptide units in a conformation favorable to charge transfer may increase faster than the number of peptide groups and thus enhance the intensity of this band. An experimental observation which is explained by the present suggestion is that for nylons the 7.5-eV band is not observed.[30] Nylons are polyamides where the peptide units are separated by a large carbon chain and therefore the charge transfer transitions are expected to occur at higher energies. In short peptides, such as dipeptides, the band is not clearly observed[6] probably because it is still too weak.

## 4. Summary and Conclusions

We carried out *ab initio* quantum chemical calculations on the vertical spectra of the molecules glycine and *N*-acetylglycine using the Complete Active Space (CAS) SCF method and multiconfigurational second order perturbation theory (CASPT2). A large number of valence and Rydberg singlet excited states have been computed.

The spectrum of glycine, the simplest amino acid, is complex due to the presence of two high-lying lone-pair orbitals. The carboxylic acid group is shown to dominate the electronic spectrum of glycine and its band scheme ressembles that of the amide group. The transitions are shifted to higher energies which is probably due to a larger electronegativity of oxygen atom as compared to nitrogen. Two $n \rightarrow \pi^*$ transitions, the $n_O \rightarrow \pi^*$ (W′ band) and the $n_N \rightarrow \pi^*$ bands, were computed as weak features at 5.65 and 6.51 eV, respectively. The two most intense transitions were found to be the $NV_1'$ and $NV_2'$ bands at 8.10 and 10.21 eV, respectively. We also computed three series of Rydberg states arising from the three highest occupied orbitals of which the most intense states are likely to correspond to the observed $R_1'$ and $R_2'$ bands in the carboxylic acids. We assigned these bands to the $n_O \rightarrow 3s$ state at 6.98 eV ($R_1'$ band) and $\pi_2 \rightarrow 3p_z$ state at 8.99 eV in glycine. The results are in agreement with experimental observations,[6,29] but do not explain the weak shoulder observed in the solid film spectra of glycine close to 8.5 eV. The latter may be assigned to the $n_N \rightarrow \sigma^*$ band computed at 8.86 eV with an intensity of one fourth of the $NV_1'$ band.

The spectrum of *N*-acetylglycine is shown to be composed of the superposition of the spectra of the chromophores forming

(31) Bensing, J. L.; Pysh, E. S. *Macromolecules* **1969**, *4*, 659.

the system: the peptide bond and the carboxylic acid group. We computed the $NV_1$ amide band at 6.76 eV, the $NV_1'$ acid band at 8.55 eV, the $NV_2$ band at 9.51 eV, and an intramolecular charge transfer state at 10.13 eV as the most intense features of the absorption spectrum. In addition, the suggested $R_1$ and $R_1'$ positions have been determined, together with a number of charge transfer states. By comparing the present results to the crystal spectrum of *N*-acetylglycine reported by Clark[11] we also find close agreement in calculated and measured transition moment directions. The absence of any evidence for a low-lying n $\rightarrow$ $\sigma^*$ band in the spectrum of *N*-acetylglycine gives further support for the assignment of the 8.5-eV band in glycine.

The present results taken together with earlier CASSCF/CASPT2 calculations on a series of simple amides do, however, not give an assignment for the intense band observed for proteins close to 7.5 eV. Earlier assignments of the 7.5-eV band to the second $\pi \rightarrow \pi^*$ $NV_2$ or $n_O \rightarrow \sigma^*$ excited states[6,10,32] appear to be very unlikely because either very large energy shifts ($\approx$1.5 eV) have to be assumed or the transition moment direction and intensity of the transition do not match. On the other hand, qualitative calculations on the acetamide dimer lead us to the conclusion that the 7.5-eV band might be due to charge transfer states involving electron transfer between neighboring peptides. The charge transfer states were calculated to be polarized parallel to the $NV_1$ states and about one third of the intensity. These characteristics are consistent with the polarized absorption spectra of poly(L-alanine),[6,31] the strong conformational dependence of the 7.5-eV band,[10] and the fact that it can not be observed in other polypeptides such as nylons.[6] To the best of our knowledge, this is the first time that charge transfer states are suggested as the origin of the 7.5-eV band. Indeed, further studies and more realistic models will be needed to investigate the effect of the conformation on the excitation energy of the charge transfer states.

(32) Demchenko, A. P. *Ultraviolet Spectroscopy of Proteins*; Springer-Verlag: Berlin, 1986.

**Acknowledgment.** The research reported in this paper has been supported by a grant from the Swedish Natural Science Research Council (NFR), by IBM Sweden under a joint study contract, by project PB94-0986 of the Dirección General de Investigación Científica y Técnica of Spain, and by the European Commission through the TMR programme. Luis Serrano acknowledges a postdoctoral grant from the DGICYT of the Ministerio de Educación y Ciencia of Spain. The authors are indebted to Prof. Björn Roos for helpful comments and discussions on the present work.

**Supporting Information Available:** Tables containing the MP2/6-31G* ground state optimized geometries for glycine and *N*-acetylglycine in $C_s$ symmetry and tables including exponents and contraction coefficients of the Rydberg basis functions for both molecules (3 pages). See any current masthead page for ordering and Internet access instructions.

JA9619972