

# EXPERIMENTAL VIBRATIONAL SPECTROSCOPIC AND THEORETICAL (*AB INITIO* CALCULATIONS) STUDIES OF THE PEPTIDE L-VAL-L-VAL

A. P. Mendham<sup>1</sup>, R. Withnall<sup>1\*</sup>, T. J. Dines<sup>2</sup> and B. Z. Chowdhry<sup>1\*</sup>

<sup>1</sup>Vibrational Spectroscopy Centre, School of Sciences, University of Greenwich, Medway Campus, Pembroke, Chatham Maritime, Kent ME4 4TB, UK; E-mail:

[b.z.chowdhry@gre.ac.uk](mailto:b.z.chowdhry@gre.ac.uk)

<sup>2</sup>Division of Physical and Inorganic Chemistry, Carnelley Building, University of Dundee, Dundee DD1 4HN, UK

**Keywords:** linear di-amino acid peptide, Gaussian, powder sample, Raman, FT-IR, deuteration

**Abstract:** Experimental Raman and FT-IR studies of protonated and deuterated powder samples of L-Val-L-Val as well as *ab initio* calculations (hybrid SCF-DFT (B3-LYP) method incorporating a cc-pVDZ basis set) have been undertaken.

The linear peptide L-Val-L-Val (Fig. 1) is an example of a molecule in which the amide (peptide) linkage is in the trans configuration.

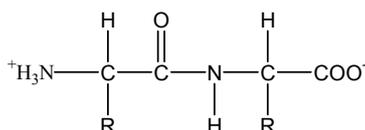


Fig. 1. Schematic diagram of the chemical structure of the linear peptide L-Val-L-Val; R = CH<sub>2</sub>CH(CH<sub>3</sub>)<sub>2</sub>.

There are, to our knowledge, no reports in the scientific literature on the vibrational spectroscopic and X-ray properties of the linear peptide L-Val-L-Val. Raman and infra-red spectra have, however, been recorded for larger, alternating peptides containing L-Val-D-Val [1]. Vibrational and X-ray studies have also been reported on other linear di-amino acid peptides such as L-Ala-Gly [2, 3] and Gly-Gly [2]. This contribution is part of a long term study of the vibrational characteristics of the cis amide conformation found in cyclic di-amino acid peptides and the trans amide conformation found in linear di-amino acid peptides.

Despite the lack of X-ray crystallographic data for L-Val-L-Val, (possibly because, as we have found from our studies, on attempts to crystallise the product is an amorphous powder) vibrational spectroscopic investigations may throw light on the hydrogen bonding properties of this molecule. For example the Raman spectrum of L-Val-L-Val only shows a very weak intensity, broad N-H stretching band located at ~3183 cm<sup>-1</sup>. This is typical for a molecule in which strong hydrogen bonding exists. The fact that no sharp Raman bands are observed in the 3300-3400 cm<sup>-1</sup> region, implies that there are no free and or very weakly hydrogen bonded N-H moieties in the powdered state, for L-Val-L-Val. Both amine and amide groups are involved in strong hydrogen bonding. This is in contrast to both L-Ala-Gly [2, 3] and L-Met-L-Met [4, 5] for which both X-ray and spectroscopic data suggest that hydrogen bonding between the amide group and its neighbouring molecules is either absent or weak. The reason for this difference in hydrogen bonding in the amide group of linear di-amino acid peptides may be due to subtle variations in molecular packing arrangements within crystals.

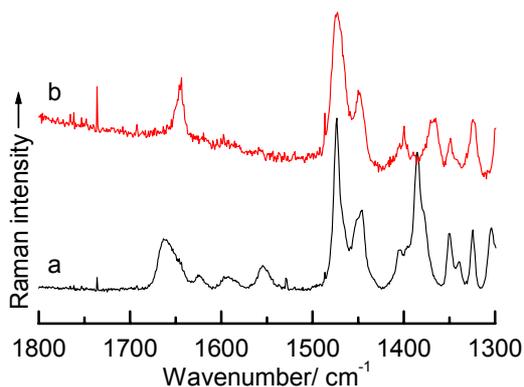


Fig. 2. Raman spectra of the linear peptide (a) L-Val-L-Val and (b) N-deuteriated L-Val-L-Val.

The broad band located at  $1659\text{ cm}^{-1}$  (Fig. 2) has been assigned to the amide I vibration of L-Val-L-Val and shows a downward shift of  $\sim 20\text{ cm}^{-1}$  after N-deuteration. This amide I deuterium shift is considerably larger than that of the trans amide I mode for L-Met-L-Met [5]. This observation suggests that there is more N-H character in the amide I normal mode of L-Val-L-Val compared to L-Met-L-Met. It is worth noting, however, that the deuterium shift found for the trans amide I band of L-Val-L-Val is considerably smaller than that of its cis amide, cyclic di-amino acid peptide, counterpart cyclo (L-Val-L-Val) which shows a downward deuterium shift of  $\sim 43\text{ cm}^{-1}$ . A characteristic  $\text{NH}_3^+$  asymmetric bending vibration is located at  $1622\text{ cm}^{-1}$ , which compares favourably with previous literature values for other di-amino acid peptides [2] and an asymmetric carbonyl stretch of the  $\text{COO}^-$  group is assigned to the Raman band at  $1590\text{ cm}^{-1}$ , which does not show a significant shift on N-deuteration.

#### Acknowledgments:

R. Withnall and B. Z. Chowdhry would like to acknowledge the EPSRC (Instrument Grant, Ref. GR/L85176) and Instruments S. A., Ltd for jointly funding the purchase of the Labram Raman spectrometer.

#### References:

1. M. Naik, *Vibrational Spectroscopy* **3** (2), 105 (1992).
2. A. M. Dwivedi, R. B. Srivastava, V. D. Gupta, *Ind. J. Pure & Appl. Phys.* **2**, 764 (1973).
3. H. J. K. Michel, G. Garriel, *Acta Crystallographica B* **26**, 410 (1970).
4. R. E. Stenkamp, L. H. Jensen, *Acta Crystallographica B* **31**, 857 (1975).
5. A. P. Mendham, R. Withnall, T. J. Dines, B. Z. Chowdhry, submitted abstract for ICORS 2004.