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

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Abstract: This contribution reports on experimental Raman and FT-IR studies of protonated and
deuteriated powder samples of L-Met-L-Met. Ab initio calculations of molecular structures and
their associated vibrational modes have also been conducted using the hybrid SCF-DFT (B3-LYP)
method incorporating a cc-pVDZ basis set.

Linear L-Met-L-Met (Fig. 1) is an example of an amino acid dimer, with the peptide (i.e.
amide) bond in the trans configuration. The terminal amino acid groups are zwitterionic [1].

![Schematic diagram of the chemical structure of L-Met-L-Met; R = CH₂CH₂SCH₃](image)

The X-ray structure of L-Met-L-Met has been reported [1], showing that the molecule
crystallises in the orthorhombic space group and that the peptide is planar. Aside from intrinsic
interest, applied interest in the physico-chemical properties of this molecule has stemmed, in part,
from its potential bacteriocidal activity [2] and involvement in cellular biosynthetic pathways [3].
Studies of L-Met-L-Met are part of a long term investigation (which also involve theoretical ab
initio calculations) of the vibrational spectroscopic properties of cis and trans amides in cyclic and
linear peptides respectively. It can clearly be seen, in Fig. 2, that there is a sharp N-H stretch located
at 3325 cm⁻¹ and a less intense, broader band located at 3213 cm⁻¹ due to the N-H group being
involved in intermolecular hydrogen bonds of different strengths. Both bands show a considerable
shift in wavenumber on N-deuteriation. Indeed it has been reported that the amine protons are
involved in strong hydrogen bonds, to the carboxyl groups [1], which is indicative of the broad N-H
stretch located at 3213 cm⁻¹. Additionally it is proposed [1] that the amide N-H’s are weakly
hydrogen bonded to the neighbouring amide carbonyl molecules and hence the presence of a sharp
vibrational band located at 3325 cm⁻¹. In the Raman spectra shown in Fig. 2, the trans amide I band
is clearly evident at 1650 cm⁻¹. This vibrational band shows a small downward shift on N-
deuteriation, of about 7 cm⁻¹ indicative of an amide I band with a small contribution from the N-H
bend. In contrast cyclo(L-Met-L-Met), in which the amide moiety adopts the cis configuration,
displays an amide I band located at 1650 cm⁻¹ [4]; upon N-deuteriation this vibrational mode shows
a downward shift of ~19 cm⁻¹.

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Fig. 2. Raman spectra of (a) L-Met-L-Met and (b) N-deuteriated L-Met-L-Met, showing the 2250-3500 and 1400-1800 cm$^{-1}$ regions.

In fact there is a distinct difference in the potential energy distribution (P.E.D.) regarding the N-H character of the cis amide I mode of cyclo(L-Met-L-Met) compared to the trans amide I band of linear L-Met-L-Met. The broad band of weak intensity at 1570 cm$^{-1}$ is assigned to the asymmetric stretch of the COO$^-$ group; this vibrational band can easily be characterized by the fact that it does not shift upon N-deuteriation. There are two other vibrational bands, in this spectral region, that show significant shifts on N-deuteriation. The first is the NH$_3^+$ bending vibration (1602 cm$^{-1}$) and the second is the amide II band at 1529 cm$^{-1}$. There is a distinct difference between the wavenumber location of the cis amide II band of cyclo(L-Met-L-Met), to the trans amide II band of linear L-Met-L-Met. The cis amide II band of cyclo(L-Met-L-Met) [4] is located at 1493 cm$^{-1}$ and its P.E.D. shows a considerably lower percentage of N-H bending character compared to its trans amide II counterpart.

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References: