

# Raman Spectroscopy of the Polymorphic Forms and Liquid State of Cocoa Butter

S. Bresson<sup>1</sup>, D. Rousseau<sup>2</sup>, S. Ghosh<sup>2</sup>, M. El Marssi<sup>3</sup>, V. Faivre<sup>4</sup>

<sup>1</sup> Laboratoire de Physique des Systèmes Complexes, Université Picardie Jules Verne, Amiens, France, <sup>2</sup> Department of Chemistry and Biology, Ryerson University, Toronto, Ontario, Canada, <sup>3</sup> Laboratoire de Physique de la matière condensée, Université Picardie Jules Verne, Amiens, France, <sup>4</sup> Equipe Physico-chimie des Systèmes Polyphasés, UMR CNRS 8612, Université Paris-Sud, Chatenay-Malabry, France.

Raman spectroscopy was used to characterize the polymorphs and liquid state of cocoa butter, with emphasis placed on the evolution of the ester carbonyl stretching ( $1800\text{-}1700\text{ cm}^{-1}$ ), along with complementary analysis and comparison of the Raman-active C-C ( $1200\text{-}1000\text{ cm}^{-1}$ ), C=C ( $1660\text{ cm}^{-1}$ ), C-H ( $3000\text{-}2700\text{ cm}^{-1}$ ) and CH<sub>2</sub> ( $1500\text{-}1250\text{ cm}^{-1}$ ) vibrational modes. Unique Raman signatures were obtained for all cocoa butter polymorphs, with their identity confirmed using differential scanning calorimetry and x-ray diffraction. The ester carbonyl region permitted polymorph discrimination due to differences in the number of modes, their relative frequencies and their full-widths at half-maximum. The C-C stretching modes, which provided insight into the trans/gauche content, were polymorph-independent. C-H stretching generally increased with polymorph stability, indicating the dominance of antisymmetric C-H methylene vibrations as the cocoa butter crystal lattice became more ordered. The change in the intensities of the C-H stretching bands used to probe the order-disorder transition of forms IV, V and VI hinted at pre-melt structural changes mostly in forms IV and V. Overall, Raman spectroscopy clearly demonstrated that the different functional groups studied could be characterized independently, allowing for the understanding of their role in cocoa butter polymorphism.

Though forms V and VI can be clearly distinguished via x-ray diffraction, we present evidence that Raman spectral characterization of the ester carbonyl stretching, C-C, C=C, C-H and CH<sub>2</sub> vibrational modes yields distinct liquid-solid and polymorph-dependent differences in CB. From a practical standpoint, the unique signatures associated with forms V and VI offers novel possibilities in the study of fat bloom formation, such as the development of predictive tools.