Selective IR-induced conformational changes of Carvacrol in solid N_2 matrix.

Leonardo J. Duarte (PQ),[1,2*] António J. L. Jesus (PQ),[2,3] Claudio M. Nunes (PQ),[2] Ataualpa A. C. Braga (PQ),[1] Rui Fausto (PQ).[3,4]

ljduarte@iq.usp.br

[1]Institute of Chemistry, Department of Fundamental Chemistry, University of São Paulo; [2] University of Coimbra, CQC-IMS, Department of Chemistry; [3] University of Coimbra, CQC-IMS, Faculty of Pharmacy; [4] Istanbul Kultur University, Faculty of Sciences and Letters, Department of Physics.

Palavras Chave: Matrix isolation, Infrared spectroscopy, Selective vibrational excitation, Conformational changes, Quantum tunneling.

Highlights

The N_2 matrix stabilizes high-energy conformers that are not found in noble gas matrices. Selective excitation of the OH stretch overtone of the lower-energy conformers generates high-energy conformers.

Abstract

Carvacrol is typically found in two different conformations based on the relative dihedral angle of the isopropyl group with respect to the hydroxyl group. Trapped inside the N_2 matrix at 15K, however, the interaction of the matrix with the hydroxyl groups stabilizes two high energy conformers as depicted in **Figure 1**. The presence of these high-energy conformers is clearly identified in the matrix by monitoring changes in the intensity of the absorption bands of the most stable conformers. These intensities increase as the CC and TC conformers decay via tunneling effects into the CT and TT conformers, respectively. The tunneling constants were experimentally determined to be equal to 8.5 x 10^{-5} (CC → CT) and 1.5 x 10^{-4} s^{-1} (TC → TT).

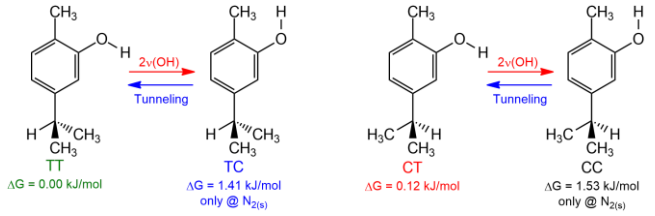

Figure 1: *Carvacrol conformers identified in solid nitrogen matrices. Gibbs energy values were obtained at B3LYP/6-311G+(2d,2p). High energy conformers decay by tunneling effects, vibrational excitation of TT and CT induces conformational changes.*

After determining the tunneling rates, the NIR spectrum of the matrix was recorded, showing a band between 7110 and 7060 cm^{-1}, which corresponds to the overlap of the conformers' first OH stretch overtone. Using an OPO laser, we irradiated the matrix with narrow-band IR radiation aiming for three distinct regions of the absorption band, as shown in **Figure 2**. The first irradiation, aiming for the left-tail of the band, (7090 cm^{-1}) triggers the conformational change CC → CT, while the second irradiation (7072 cm^{-1}) didn't trigger any conformational change, therefore, the observed difference spectrum shows only tunneling effects. The final irradiation triggers both CC → CT and TC → TT processes, indicating the excitation of both lower energy conformers. As conclusion, by selecting the proper wavelength one can selectively trigger a conformational change.

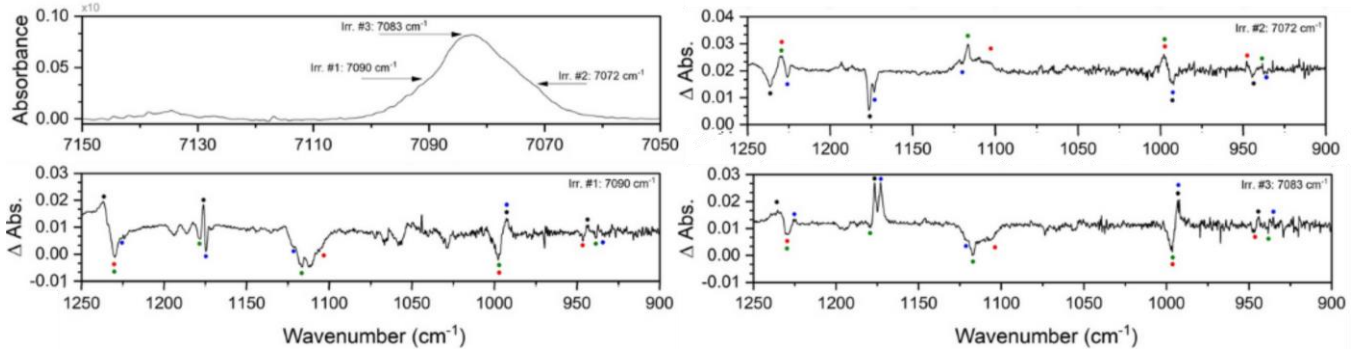

Figure 2: *Top left panel: NIR spectrum in the region of the OH stretch overtone showing the three irradiation experiments. Other panels: Difference spectra after each irradiation.* • *= TT,* • *= TC,* • *= CT,* • *= CC.*

Acknowledgments

L. J. D. and A. A. C. B are grateful to FAPESP for financial support (fellowship #2022/09269-1, #2023/13220-0 and #2015/01491-3) and CNPq for academic support (grant #313720/2023-1). CQC-IMS is supported by FCT, through Projects UIDB/00313/2025 and UIDP/00313/2025 and LA/P/0056/2020. The ERA Chair Spectroscopy@IKU is funded by the European Research Agency under HORIZON-WIDERA-2023-TALENTS-01 (Grant No. 101184899).