

FAR-IR ACTION SPECTROSCOPY OF AMINOPHENOL AND ETHYLVANILLIN: EXPERIMENT AND THEORY

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Investigations of molecular structure and conformational isomerism are at the forefront of today's biophysics and biochemistry. In particular, vibrations excited by far-IR radiation can be highly sensitive to the molecular 3D structure as they are delocalized over large parts of the molecule. Current theoretical predictions of vibrational frequencies in the far-IR range are not accurate enough because of the non-local character and anharmonicity of these vibrations. Therefore experimental studies in the far-IR are vital to guide theory towards improved methodology.

In this work we present the conformer-specific far-IR spectra of aminophenol and ethylvanillin molecules in the range of 220-800 cm^{-1} utilizing ion-dip action spectroscopy carried out at the free electron laser FELIX in Nijmegen, Netherlands. The systems studied are aromatic molecules with important functional groups such as the hydroxyl (OH) and amino (NH_2) groups in aminophenol, and the hydroxyl, ethoxy (OCH_2CH_3) and formyl (CHO) groups in ethylvanillin. The experimental spectra show well resolved conformer-specific vibrational bands. In the case of ethylvanillin only two planar conformers have been observed under supersonic jet expansion conditions. Despite the fact that these conformers differ only in the position of oxygen of the formyl group with respect to ethoxy group, they are well distinguishable in far-IR spectra.

The capability of numerical methods based on density functional theory (DFT) for predicting vibrational frequencies in this spectral region within the harmonic approximation has been investigated by using several hybrid-functionals such as B3LYP, PBE0, B2PLYP and CAM-B3LYP. An anharmonic correction based on vibrational second order perturbation theory approach^a was also applied. We have found that the methods we considered are well suited for the assignment of far-IR vibrational features except the modes which are strongly anharmonic, like the NH_2 wagging mode in aminophenol which is likely to be due to double well potential governing this motion.

^aV. Barone, Anharmonic vibrational properties by a fully automated second-order perturbative approach, *J. Chem. Phys.* 122 (2005) 014108.