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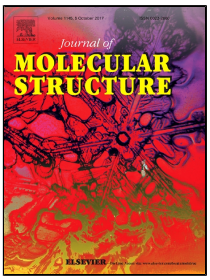

Improved Assignments of the Vibrational Fundamental Modes of *ortho*-, *meta*-, and *para*-xylene Using Gas- and Liquid-Phase Infrared and Raman Spectra Combined with *ab initio* Calculations: Quantitative Gas-Phase Infrared Spectra for Detection

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Improved Assignments of the Vibrational Fundamental Modes of *ortho*-, *meta*-, and *para*-xylene Using Gas- and Liquid-Phase Infrared and Raman Spectra Combined with *ab initio* Calculations: Quantitative Gas-Phase Infrared Spectra for Detection

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Abstract. Xylenes contain a blend of the *ortho*-, *meta*-, and *para*- isomers, and all are abundant contaminants in the ground, surface waters, and air. To better characterize xylene and to better enable its detection, high quality quantitative vapor-phase infrared spectra of all three isomers over the 540-6500 cm^{-1} range are reported. All fundamental vibrational modes are assigned based on these vapor-phase infrared spectra, liquid-phase infrared and Raman spectra, along with density functional theory (DFT), *ab initio* MP2 and high energy-accuracy compound theoretical model (W1BD) calculations. Both MP2 and DFT predict a single conformer with C_{2v} symmetry for *ortho*-xylene, and two conformers each for *meta*- and *para*-xylene, depending on the preferred orientations of the methyl groups. For *meta*-xylene the two conformers have C_s and C_2 symmetry, and for *para*-xylene these conformers have C_{2v} or C_{2h} symmetry. Since the relative population of the two conformers is approximately 50% for both isomers and predicted frequencies and intensities are very similar for each conformer, an arbitrary choice to discuss the C_s conformer for *meta*-xylene and the C_{2v} conformer for *para*-xylene is made. Integrated band intensities for all isomers are reported. Using the quantitative infrared data, the global warming potential values of each isomer are determined. Potential bands for atmospheric monitoring are also discussed.

1. Introduction

Xylene (xylol or dimethylbenzene, $(CH_3)_2C_6H_4$) has a central benzene ring with two methyl groups attached as substituents and whose relative position distinguish the three isomers *ortho*-, *meta*-, and *para*-xylene. It occurs naturally in petroleum and coal tar [1-3], but xylene is primarily a synthetic chemical, being produced by the chemical industry from petroleum. Xylene is an aromatic compound discovered as a constituent of wood tar and was first isolated and named by the French chemist Auguste Cahours in 1850 [4]. Nearly a century later, Pitzer and Scott [5] made thermodynamic measurements of the three xylenes such as melting points, vapor pressures up to 60 ºC, and heat capacities of the vapors. Being the second most important aromatic product in terms of consumption for the chemical industry after benzene, mixed xylenes contain a blend of *ortho*-, *meta*-, and *para*- isomers as well as other components such as ethylbenzene. This equilibrium mixture of isomers is the feedstock from which the desired component is isolated [6-