EXAMINING INTERMOLECULAR INTERACTIONS BETWEEN HYDROCARBONS AND WATER: A BROADBAND ROTATIONAL SPECTROSCOPIC STUDY OF THE α-PINENE – WATER COMPLEX

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Released into the atmosphere by vegetation, biogenic volatile organic compounds (VOCs) contribute substantially to yearly carbon emission, amounting to approximately 1150 Tg of carbon per year.[1] α-pinene, a bicyclic monoterpene, is not only one of the most abundant biogenic VOCs released, but also plays a critical role in the generation of secondary organic aerosol. Once released, α-pinene can be photo-oxidized by atmospheric species such as ozone or various radical species.[2] Water is relatively abundant in the atmosphere and has therefore a high probability of a close contact with α-pinene. Complexation with water may affect the reactivity with species such as ozone, thus altering product yield, and ultimately the rate of aerosol formation. It is difficult to predict a preferred structure for the α-pinene-water cluster using chemical intuition alone, and a study of its structure and energetics can provide insights into intermolecular interactions between weakly-polar hydrocarbons and hydrogen bonding capable species, as well as data relevant to atmospheric processes. To experimentally identify α-pinene-water clusters we used a chirped pulse Fourier transform microwave spectrometer in the 2-6 GHz range[3] and the experiments were supplemented with electronic structure calculations. Two potential conformers were theoretically identified, both of which involve the formation of an O-H — π bond between water and α-pinene. However, only the higher energy conformer could be assigned experimentally. From various one-dimensional energy scans along internal rotation coordinates, the absence of the lower energy conformer is most likely due to a large amplitude O-H wagging motion, which leads to a partial dipole moment cancellation. The O-H — π interaction in both complexes was then visualized and quantified using non-covalent interactions[4] and natural bond orbital analyses[5], respectively.

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