

THE 3-METHYLCATECHOL-(H₂O)_{N=1-4} COMPLEXES: STUDYING MICROSOLVATION USING BROADBAND ROTATIONAL SPECTROSCOPY

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Biomass burning greatly influences the Earth-cloud-climate system by releasing complex mixtures of organic and inorganic species into the atmosphere.¹ During biomass burning, lignin, an organic polymer and a major component of wood,² undergoes pyrolysis resulting in the direct release of substituted catechols.³ 3-methylcatechol (3MC), a common substituted catechol, may be photo-oxidized or aggregates with other atmospherically relevant molecules, such as water, forming small molecular clusters or hydrates. These hydrates play an important role in the early phases of aerosol particle formation, and can provide valuable thermodynamic data for modelling. To elucidate the conformationally complex hydrate structures we analyzed rotational spectra measured with a chirped-pulse Fourier transform microwave spectrometer in the 2-6 GHz range.⁴ To aid in spectral assignment, we used the Conformer–Rotamer Ensemble Sampling Tool (CREST)⁵ to generate an ensemble of conformers. Two monomer conformations with their respective ¹³C isotopologues were assigned, followed by the determination of substitution structures and semi-experimental effective structures. With the aid of the CREST results, transitions of several hydrates, 3MC-(H₂O)_{N=1-4}, were also assigned in the experimental spectrum. For the monohydrate and dihydrate, splittings of rotational transitions into quartets were observed. These splittings are a consequence of methyl internal rotation (MIR) and the proton exchange motion of water. Only MIR splittings are present for the trihydrate, while no MIR or proton exchange splitting is present for the tetrahydrate. Non-covalent interactions⁶ and natural bond orbital analyses⁷ were used to visualize and quantify the intermolecular interactions within each cluster. 1. M. Fromm et al., *J. Geophys. Res. Atmospheres*, 2019, 124, 13254–13272.; 2. A. V. Bridgewater, *Therm. Sci.*, 2004, 8, 21–50.; 3. M. Asmadi et al., *J. Anal. Appl. Pyrolysis*, 2011, 92, 88–98.; 4. N. A. Seifert et al., *Phys. Chem. Chem. Phys.*, 2018, 20, 27630–27637.; 5. P. Pracht et al., *Phys. Chem. Chem. Phys.*, 2020, 22, 7169–7192.; 6. J. Contreras-García et al., *J. Chem. Theory Comput.*, 2011, 7, 625–632.; 7. E. D. Glendening et al., *J. Comput. Chem.*, 2013, 34, 1429–1437.