# Rotational Spectra and *ab initio* modeling of dicarboxylic acids: Succinic Acid

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Atmospheric aerosols affect terrestrial visibility by absorbing and reflecting incoming solar radiation, and they also influence climate and alter human health. Aerosols can be directly emitted from natural and anthropogenic sources or formed directly in the atmosphere through nucleation from gas phase species. New particle formation events have been observed frequently and worldwide but it is not fully understood how particles form at molecular level, creating one of the largest sources of uncertainty in atmospheric models and climate predictions (Zhang, 2010).

Several mechanisms have been proposed to explain nucleation events in the continental troposphere, including binary $H_2SO_4/H_2O$ and ternary $H_2SO_4/H_2O/NH_3$ nucleation, ion-mediated nucleation, and nucleation enhanced by organic compounds (Metzger et al., 2010). In particular, dicarboxylic acids present in the troposphere have been proposed as favorable candidates to enhance the formation of the critical nucleus, as one of their carboxylic groups would be strongly hydrogen-bonded to $H_2SO_4$, whereas the free –COOH group would allow the growth of the complex until an aerosol particle is formed (Xu and Zhang, 2010; Gao-Lei Hou et al., 2013).

As a first step in exploring the configuration of the critical nucleus, we have conducted a rotational spectroscopic study of succinic acid (SA), which is a relatively simple dicarboxylic acid that has been detected in the troposphere. Rotational spectroscopy provides the most accurate vision of the molecular structure through precise moments of inertia.

In this work, we have applied the technique of Fourier Transform Microwave Spectroscopy (FTMW) in a supersonic jet, which is a high sensitivity and resolution technique. Expansion of a gaseous sample in a supersonic jet allows rapid cooling of the sample to only a few Kelvin so most molecules relax to the lowest ro-vibrational energy levels. SA was vaporized by UV ultrafast laser ablation avoiding any decomposition of the sample via heating conventional methods (Cocinero et al., 2012). The vaporized sample was seeded into an expanding stream of Ne forming a supersonic jet, where the molecules were probed by time-domain rotational spectroscopy. The experimental study was supplemented by *ab initio* (MP2) and DFT (M062X and B3LYP) calculations describing the conformational landscape and rotational parameters.

The rotational spectrum detected the presence of a single most stable conformation, for which accurate rotational and centrifugal distortion parameters have been determined. The rotational parameters were found in good agreement with the predictions for the predicted global minimum. The study was extended to all monosubstituted isotopic species ($^{13}C$, $^{18}O$, D(O)), which were positively identified, leading to an accurate determination of the effective and substitution structures of the molecule, and hence, we were able to accurately determine all bond lengths, valence and dihedrals angles.

The next step of this study will be to detect intermolecular complexes formed by succinic acid and sulfuric acid. The ultimate goal is to provide experimental microscopic evidence of the geometric arrangement and energetic stability of a feasible critical nucleus to account for new particle formation in the atmosphere.

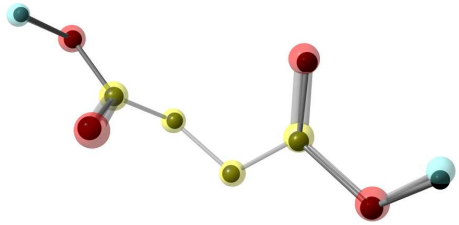

Figure 1: A comparison of the substitution and *ab initio* structures of SA. The full molecular structure is the theoretical structure. The smaller dark spheres are the experimental atom positions.

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