CHARACTERIZATION OF MICROSOLVATED CROWN ETHERS FROM BROADBAND ROTATIONAL SPECTROSCOPY

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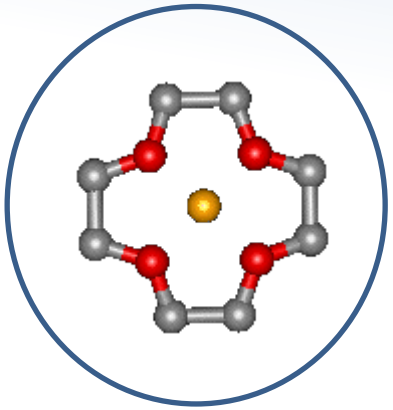
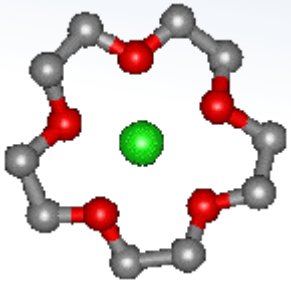
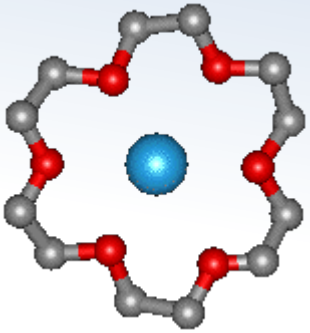
Crown Ethers



12C4



15C5



18C6

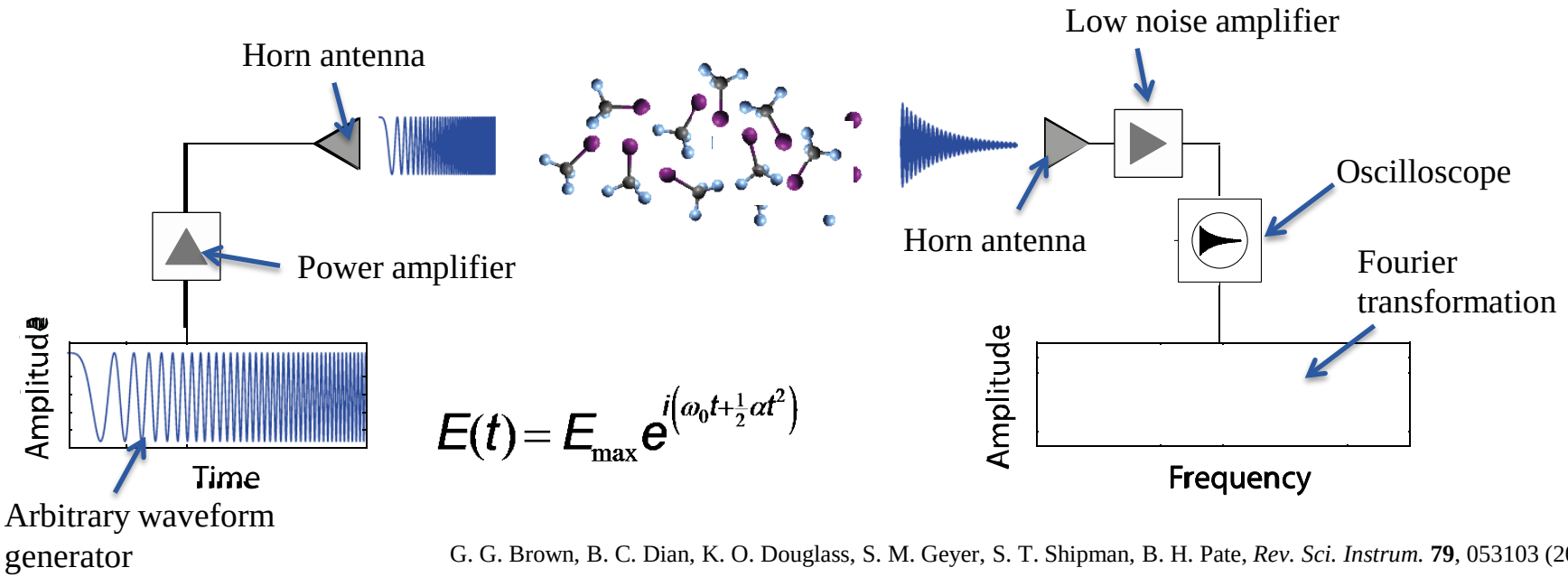
- ✓ Cyclic Ethers: the most common formed by repetition of ethylene oxide units
- ✓ High Selectivity binding alkali cations, Li^+, Na^+ and K^+
- ✓ High conformational flexibility due to rotation about single bonds
- ✓ Structural changes and conformational preferences under microsolvation

Previous Studies

- ✓ Pioneering work was performed on benzo-crown ether compounds using IR-UV laser spectroscopy techniques in supersonic jets.
  - Shubert *et al. J. Phys. Chem. A* **2009**, *113*, 8055–66; **2009**, *113*, 8067–79 (Purdue)
  - Kusaka *et al. Phys. Chem. Chem. Phys.* **2007**, *9*, 4452–9; **2009**, *11*, 9132–9140; **2011**, *13*, 6827–36. (Hiroshima)
  - For benzo-15-crown-5 a single water changed the energy order of the respective crown conformations. Two water molecules bind to the opposite side of the crown ring.
- ✓ Microwave spectrum of 15C5.
  - Gamez *et al*. *J. Phys. Chem. Lett.* **2012**, *3*, 482–485; *Phys. Chem. Chem. Phys.* **2012**, *14*, 12912. (Valladolid Univ.)
  - 8 forms observed
- ✓ (IRMPD) vibrational spectroscopy – hydronium and ammonium cation complexes
  - P. Hurtado, F. Gámez, S. Hamad, B. Martínez-Haya, J. D. Steill, J. Oomens, *J. Phys. Chem. A* **2011**, *115*, 7275–7282

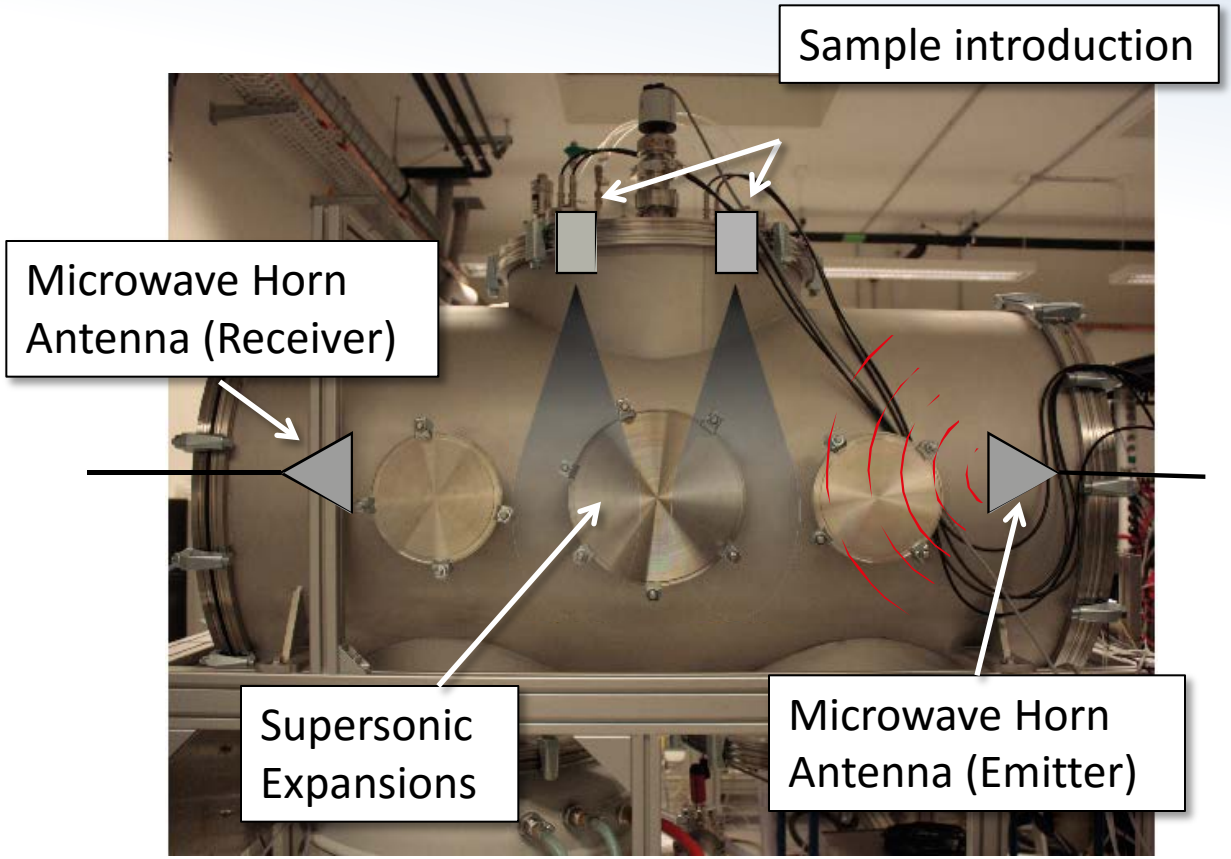
Experiment

- Chirped Pulse Microwave Spectroscopy
  1. Generation of a chirped microwave pulse (4 μs, 2-8 GHz, eight frames) and excitation of a molecular ensemble.
  2. Polarization starts to decay after the pulse.
  3. Recording of the Free Induction Decay (FID).



G. G. Brown, B. C. Dian, K. O. Douglass, S. M. Geyer, S. T. Shipman, B. H. Pate, *Rev. Sci. Instrum.* **79**, 053103 (2008

Experiment



- 2-8 GHz bandwidth
- 20 kHz resolution
- 32 Hz repetition rate

Summary

- Broadband rotational spectroscopy is a extraordinary tool for structural studies of microsolvated crown ethers.

- Unambiguous characterization based on the observation of isotopologues

  - ✓ Natural abundance ^{13}C
  - ✓ Enriched sample ^{18}O

- Water alters the PES surface of the ether upon cluster formation.

- Complexation of two water molecules on same side (12C4 and 15C5) or both sides (15C5) and no water-water interactions

- First observation of the water cluster of 18C6

Acknowledgement

- **Thank you for your attention!**

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