A CHIRPED PULSE FTMW STUDY OF THE STRUCTURE OF PHENOL DIMER

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Phenol dimer has been studied extensively and is considered a benchmark molecular complex for *ab initio* theory due to a long range dispersion interaction between the rings as well as an intermolecular hydrogen bond. Previously, the structure had been determined using RCS[a,b] and high resolution UV measurements;[c] however, several assumptions were integrated into the structure because a full isotopically substituted structure could not be determined. In this study, the rotational spectrum of the dimer as well as ^{13}C and ^{18}O isotopologue spectra that were seen in natural abundance were obtained using chirped pulse Fourier transform microwave spectroscopy (CP-FTMW). The structure was determined using both linear least squares fitting (r_0 structure) and the Kraitchman substitution analysis (r_s structure). *Ab initio* calculations were performed for the dimer using MP2/cc-pVTZ cp[d], B3LYP/6-31G(d,p), M06-2X/6-31G(d,p), and M06-2X/6-311++G(d,p), while CCSD calculations are currently under way. Changing the level of theory and the basis set dramatically changes the structure. The MP2 calculation underestimates the hinge angle (C-O-O-C dihedral angle), while the B3LYP overestimates it. The M06-2X calculations seem to give the best cost-to-benefit ratio when compared to the r_s structure, but they show poorer agreement with increasing basis set size.

[a] L. L. Connell, S. M. Ohline, P. W. Joireman, T. C. Corcoran, and P. M. Felker, J.Chem.Phys. 96, 2585 (1992)
[b] A. Weichert, C. Riehn, and B. Brutschy, J. Phys. Chem. A 105, 5679 (2001)
[c] M. Schmitt, M. Böhm, C. Ratzer, D. Krügler, K. Kleinermanns, I. Kalkman, G. Berden, and W. L. Meerts, Chem. Phys. Chem. 7, 1241 (2006)
[d] P. Jurecka, J. Sponer, J. Cerny, and P. Hobza, Phys. Chem. Chem. Phys. 8, 1985 (2006)