DETECTION AND ANALYSIS OF ROTATIONALLY RESOLVED TORSIONAL SPLITTINGS IN PHENOL (C_6H_5OH): THE HIGH RESOLUTION FTIR SPECTRUM OF PHENOL BETWEEN 600 AND 1300 CM^{-1}

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One of the great challenges of high resolution infrared spectroscopy is to understand the rovibrationally resolved spectra and dynamics of large molecules involving numerous degrees of freedom and large amplitude motions like bending, torsion or inversion modes[a]. Complicated resonance networks can be built up through the coupling of such modes and the energy flow can be studied upon excitation[bc]. Excellent examples of the study of such phenomena are the FTIR spectra of aromatic systems which can now be rovibrationally resolved using state-of-the-art technology[d]. As a benchmark molecule we shall discuss phenol. Its vibrational spectrum has already been assigned at low resolution[e] and its photodissociation has been studied recently[f]. Its rotationally resolved infrared spectrum has now been recorded in the range 600–1300 cm^{-1} with our Bruker ZP2001 spectrometer with a resolution of better than 0.001 cm^{-1}. This spectrum was used in an analysis of the out-of-plane modes ν_4 ($\tilde{\nu}_0$ = 687.00544 cm^{-1}) and ν_{17b} ($\tilde{\nu}_0$ = 881.70033 cm^{-1}). Here, no torsional splittings or resonances were observed, as opposed to the spectrum of the a-type bands ν_{12} (OH-sensitive), $2\nu_{18b}$ (OH-sensitive), ν_{7a} (CO-stretch), β (OH-bend) and the combination bend $\nu_{17b} + \tau$ (CH-bend + torsion). We will discuss the J-dependent doublets with splittings ranging from 0.01 to 0.04 cm^{-1} observed in the rovibrational spectra, and will present an analysis of the combination band $\nu_{17b} + \tau$ with band centers of the two torsional components $\tilde{\nu}_{0a}$ = 1198.24163 cm^{-1} and $\tilde{\nu}_{0b}$ = 1198.20114 cm^{-1}. A comparison between the phenol and fluorobenzene spectra will also be presented.

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