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Title:Broadband rotational spectroscopy of acrylonitrile: Vibrational energies from perturbations

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Abstract:The coverage of the room-temperature rotational spectrum of acrylonitrile has been expanded to a total of 1170 GHz, by recording broadband spectral segments at frequencies ranging 90-1900 GHz. This corresponds, in total, to 61.6% coverage of the rotational spectrum up to 1.9 THz and facilitated an in depth study of rotational transitions in the lowest vibrational states of acrylonitrile and up to large values of rotational quantum numbers. Multiple perturbations between the four lowest vibrational states of the molecule have been identified and successfully fitted within the framework of a coupled four state Hamiltonian. The fit encompasses over 12 500 measured transition frequencies, and delivers precise wavenumbers for the three lowest excited vibrational states entirely on the basis of perturbations in the rotational spectrum: $\nu_{11} = 228.29986(2)$, $\nu_{15} = 332.67811(2)$, and $2\nu_{11} = 457.17496(2)$ cm^{-1}. The new results are compared with ab initio anharmonic force field calculations and the techniques used to deal in an efficient manner with a broadband, high-resolution spectrum of this type are also described in some detail. © 2012 Elsevier Inc. All rights reserved.

Techniques of analysis - THz-spectrum - Vibrational energies