HIGH-RESOLUTION FTIR SPECTROSCOPY OF BENZALDEHYDE IN THE FAR-INFRARED REGION: PROBING THE ROTATIONAL BARRIER

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A discrepancy between theoretical and experimental values of the rotational barrier in benzaldehyde has been observed, which was attributed to inaccurate experimental results in part.[a] Here, we report results on the –CHO torsion of benzaldehyde (C_6H_5CHO) based on a high resolution spectroscopic investigation in the far-infrared range in an effort to remove the experimental ambiguity. The rotationally-resolved vibrational spectra were measured with an unapodized resolution of 0.00064 cm^{-1}using synchrotron-based Fourier transform infrared (FTIR) spectroscopy at the Canadian Light Source. The torsional fundamental ν_t = 109.415429(20) $\mathrm{cm}^{-1}$was unambiguously assigned via rovibrational analysis, followed by the tentative assignment of the first $(2\nu_t - \nu_t)$ and second $(3\nu_t - 2\nu_t)$ hot bands at 107.58 $\mathrm{cm}^{-1}$and 105.61 cm^{-1}, respectively, by comparison of the observed Q branch structures at high resolution with simulation based on a previous microwave study.[b] This assignment is different from any previous low resolution infrared studies in which the intensity patterns were misleading. The key result of the assignment of the first three transitions allowed for the determination of the barrier to internal rotation of (hc)1533.6 cm^{-1}(4.38 kcal mol^{-1}). When compared with calculated results from vibrational second-order perturbation theory (VPT2) and quasiadiabatic channel reaction path Hamiltonian (RPH), the experimental value is still too low and this suggests that the discrepancy between theory and experiment remains despite the best experimental efforts.

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[a] I.A. Godunov, V.A. Bataev, A. V. Abramenkov, V.I. Pupyshev, *J. Phys. Chem.A*, **2014**, 118, 10159-10165, and references therein.

[b] R. K. Kakar, E. A. Rinehart, C. R. Quade and T. Kojima, *J. Chem. Phys*, **1970**, 52, 3803-3813